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CHEMICAL REACTIONS AND THEIR EQUATIONS

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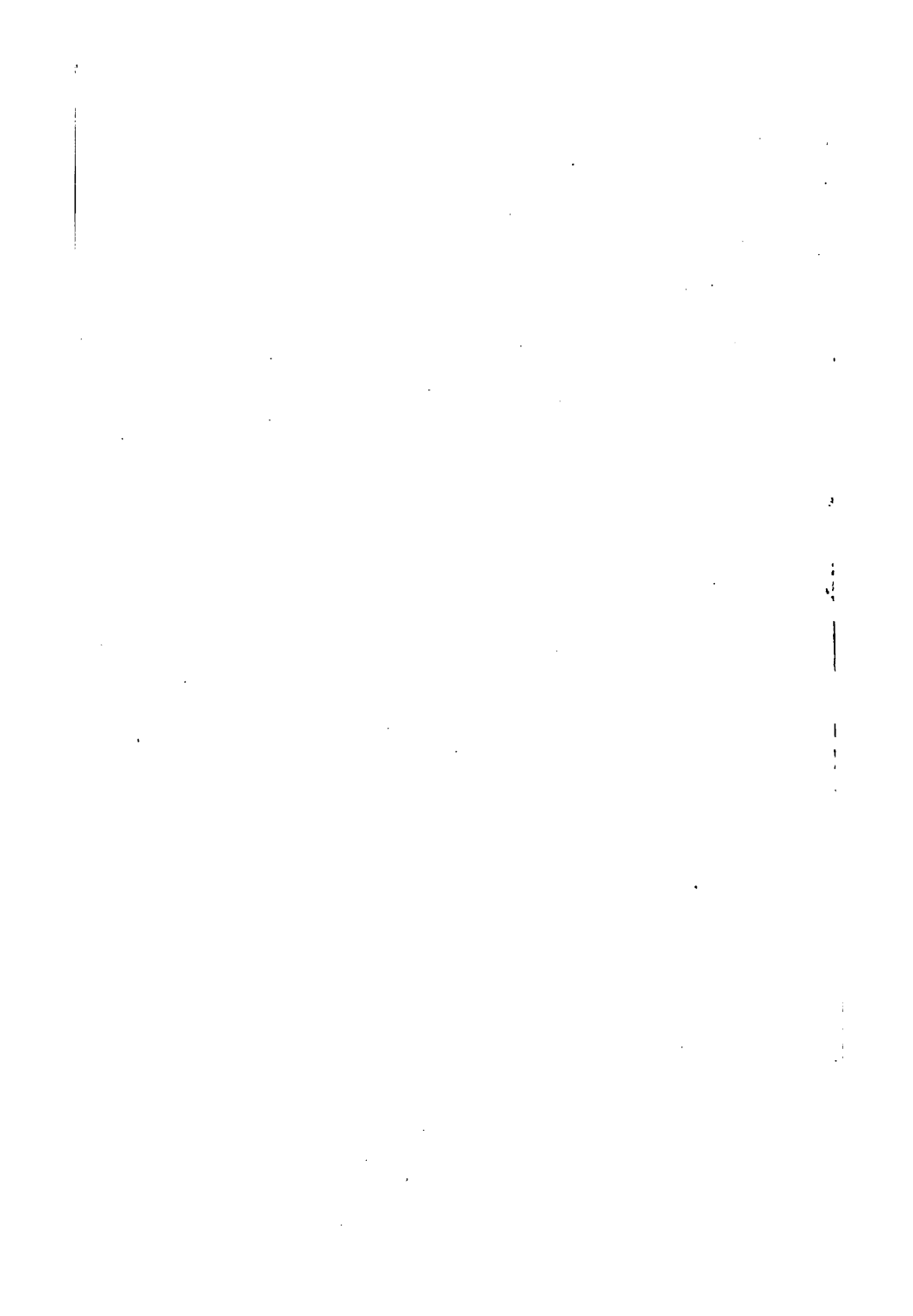


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CHEMICAL REACTIONS
AND THEIR EQUATIONS

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CHEMICAL REACTIONS AND THEIR EQUATIONS

A Guide and Reference Book
for Students of Chemistry

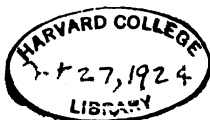
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PREFACE

The inability to balance a chemical equation is a most common difficulty of students of chemistry. The writer when teaching at a large university actually encountered graduate students of chemistry who were unable to balance an incomplete ionic equation that involved oxidation and reduction, not to mention the large number of first and second year students who had only a very hazy idea of the principles.

In order to supply students with necessary material and to expound the general principles of balancing equations, this concise volume was written. It does not enter into a detailed discussion of physico-chemical equations, but confines itself mainly to a consideration of purely chemical equations from a technical and arithmetical standpoint. The writer hopes that a study of this volume, (which, to the writer's knowledge, is the only one of its kind on the subject) in connection with any good text, will aid toward a clearer understanding of chemistry on the part of the student. A detailed study of the following pages should enable anyone to balance any chemical equation rapidly and correctly.

With pleasure the writer acknowledges his gratitude to Dr. Henry D:Arcy Power for many valuable suggestions and criticisms in reading the manuscript, and to his students, Messrs. Jordan, Konrad, and Magee for reading the manuscript and proofs. He also feels much indebted to his teachers, Profs. Edmond O'Neill, G. N. Lewis, and Joel H. Hildebrand.

I.W.D.H.

SAN FRANCISCO, CAL.

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CHEMICAL REACTIONS AND THEIR EQUATIONS

CHAPTER I

SYMBOLS

ERRATA

Page 3: line 13. Place comma after "therefore" and take out comma after "atom."

Page 101, equation No. 429. Read Zn^{++} instead of Zn^{--} .

Page 112, in table of atomic weight read 175.0 instead of 17.50 for Lutecium.

Page 112, line 8, read an instead of n.

English prices:

Page 47, question 27, last sentence would read: Fe costs 3d, Al = sh. 1.3d, and Mg = sh. 1.6d.

Page 45, question 2. Price of Zn = 2 sh.

HACKER, CHEMICAL REACTIONS AND THEIR EQUATIONS.

THUS ATOMS OF ONE NATURE COMBINE TO FORM AN elemental molecule and aggregate to an element, while unlike atoms combine to form a compound molecule and aggregate to a compound. Molecules are capable of independent existence, that is, they may exist separately and not in aggregation with similar molecules. Thus a molecule is the smallest imaginable particle of a compound, an atom the smallest imaginable particle of an element. While atoms are chemically inde-

structible,¹ the molecules are susceptible to endless chemical change. Such changes and interchanges are expressed in the form of chemical equations.

A chemical symbol has three distinct uses as it may represent an *atom*, *molecule* or *ion*. To distinguish whether a symbol represents an atom, molecule, or ion a numeral or + or - sign is used.

Atom.—The *atom* of an element is shown by the symbol alone. Thus H represents an atom of hydrogen with an atomic weight of 1.008; Cl stands for an atom of chlorine with an atomic weight of 35.45, and Fe is an atom of iron (ferrum) with atomic weight 56.5.

Molecule.—The *molecule* of an element is shown by the symbol with a small numeral attached indicating the number of atoms: H_2 or H^2 is a molecule of hydrogen containing two atoms of hydrogen, the molecular weight being the sum of the atomic weight = $2 \times 1.008 = 2.016$; S_4 or S^4 is a molecule of sulfur containing four atoms of sulfur, the molecular weight being $4 \times 32.00 = 128.00$; S_6 or S^6 is a molecule of sulfur with six atoms of sulfur, the molecular weight of this molecule is $6 \times 32.00 = 192.00$; S_x or S^x is a molecule of sulfur containing an unknown number of atoms of sulfur. All gaseous elements have ordinarily two atoms in their molecule, *e.g.* O_2 , N_2 , Cl_2 , which indicates respectively a molecule of oxygen, nitrogen, and chlorine as gases.

¹ The fact that atoms are chemically indestructible does not exclude the possibility that they may be transformed by physical means. Modern research, both theoretical and practical, point to still smaller corpuscles or electrons as the building stones of atoms. Nevertheless the conception of a "structure of the atoms" will not affect the older conception of an atom as the "chemical unit," or an element as a type of atoms. Chemists will thus continue to deal with atoms, and future progress in the subatomic realm will merely increase the knowledge of the relation among elements and their probable evolution, but will not materially change the application of the atomic theory.

Only in a few cases have the number of atoms in a molecule been determined for solid elements, *e.g.* P_4 , P_8 , As_2 , As_4 . If the number of atoms in a molecule of a solid element is unknown, the molecule should be written with x , *e.g.* Na_x , Fe_x , Al_x , C_x . However, in metals, this number is assumed to be one, so that in this case Na would represent not only an atom, but also a molecule of sodium (natrium).

Ion.—The *ion* of an element is indicated by the symbol with one or more positive(+) or negative (−) signs attached, which represent the number of positive or negative charges attached to the atom of an element. An ion, therefore, is an electrified atom or an atom with a certain number of electrical corpuscles attached. These charges are also written as dots and dashes, thus: H^+ or $H^{\cdot}$ = hydrogen ion, H-atom with one positive charge, Cl^- or Cl' = chloride ion, Cl-atom with one negative charge, Ca^{++} or $Ca^{\cdot\cdot}$ = calcium ion, Ca-atom with two positive charges, S^{--} or S'' = sulfide ion, S-atom with two negative charges, Al^{+++} or $Al^{\cdot\cdot\cdot}$ = aluminum ion, Al-atom with three positive charges. These ions ordinarily exist only in solutions. The majority of salts dissolved in water become ionized because their component atoms become electrified. Thus $NaCl$ (sodium chloride) when dissolved in water will form Na^+ (sodium ion) and Cl^- (chloride ion), while a small amount of the original sodium chloride remains as $NaCl$ (molecular or non-ionized sodium chloride). Some salts will ionize slightly, that is, they will break apart (dissociate) only to a small degree. Ammonium chloride (NH_4Cl) when dissolved in water forms a few ammonium ions (NH_4^+) and a few chloride ions (Cl^-)—the larger percentage of the substance remaining in molecular combination (NH_4Cl).

Ionization or electric dissociation, therefore, is the breaking apart of the molecule in solution whereby the atoms or groups of atoms (radicals) acquire a positive or negative charge. It must be borne in mind that the properties of the ions are distinctly different from the properties of the atoms. Sodium is different from sodium ion, iron metal (Fe) differs from ferrous ion (Fe^{++}) and ferric ion (Fe^{+++}), for the ions are always electrified or charged atoms.

Summary.—The three ways of using a chemical symbol are summarized as follows:

- H = *one hydrogen atom*, which exists in compounds,
- 2H = *two hydrogen atoms*,
- H_2 = *one hydrogen molecule*, which exists in hydrogen gas,
- 2H_2 = *two hydrogen molecules*,
- H^+ = *one hydrogen ion*, which exists in the solution of acids,
- 2H^+ = *two hydrogen ions*.

Accordingly the symbols Cl, S, 2S, 3S, Fe, Al, stand respectively for one atom of chlorine, one atom of sulfur, two atoms of sulfur, three atoms of sulfur, one atom of iron, one atom of aluminum, while their respective atomic weights; Cl_2 , S_6 , 2S_6 , 3S_6 , Fe_x , Al_x , means one molecule of chlorine (two atoms), one molecule of sulfur (six atoms), two molecules of sulfur (twelve atoms), three molecules of sulfur (eighteen atoms), one molecule of iron (unknown number of atoms), one molecule of aluminum (unknown number of atoms); Cl^- , S^{--} , 2S^{--} , 3S^{--} , Fe^{++} , Fe^{+++} , Al^{+++} , represent respectively one chloride ion (chlorine atom with one negative charge), one sulfide ion (sulfur atom with two negative charges), two sulfide ions (two sulfur atoms with four

negative charges), three sulfide ions (three sulfur atoms with six negative charges), one ferrous ion (one iron atom with two positive charges), one ferric ion (one iron atom with three positive charges), one aluminum ion (one aluminum atom with three positive charges).

QUESTIONS

1. Define symbol, atom, molecule, ion, ionization.
2. What is the symbol for an atom of bromine, selenium, potassium, nitrogen, copper, magnesium, phosphorus?
3. What is the symbol for a molecule of the elements given in question 2?
4. What is the symbol for an ion of the elements given in question 2?
5. What is the difference between N_2 and $2N$, O_2 and O , $3O_2$, $2O$, and $6O$, F_2 , $2F^-$ and $2F$?
6. State all the information contained in the symbols: Na , Na^+ , Se , Se_4 , Se^{--} , C , As , As_2 , As_4 , Hg , Hg^+ , Hg^{++} .

CHAPTER II

FORMULAS

Formula.—The vocabulary of chemistry consists of formulas. A chemical formula is a combination of symbols which shows the number and kind of atoms in a molecule, hence, the formula tells the chemical composition of a substance and represents the molecule of a compound. However, as the symbols not only indicate the kind of atom, but also a certain quantity, called the atomic weight, it is evident that a formula must also include the quantitative composition of a compound, and the molecular weight.

For instance, NaCl means a molecule of sodium chloride containing one atom of sodium or 23 parts by weight, and one atom of chlorine or 35.5 parts by weight. The total or molecular weight is naturally the sum of the atomic weights, that is, $23 + 35.5 = 58.5$. From this proportion the percentage can be calculated, for as 58.5 parts of sodium chloride contain 23 parts of sodium, then $58.5 : 23 :: 100 : x$, and $x = 23 \times 100 / 58.5 = 39.3$ that is 39.3 per cent sodium; while the percentage of chlorine is found by the proportion $58.5 : 35.5 :: 100 : x$, and $x = 35.5 \times 100 / 58.5 = 60.7$ which means 60.7 per cent of chlorine. Two molecules of sodium chloride may be written either 2NaCl or $(\text{NaCl})_2$. In the first case the two in front refers to the whole following formula, in the second case the parenthesis is necessary as, otherwise, the formula NaCl_2 would indicate a compound molecule containing one atom of sodium and two atoms of chlorine which is wrong.

Na_2SO_4 means one molecule of sodium sulfate containing two atoms of sodium or $2 \times 23 = 46$ parts of sodium,
 one atom of sulfur or 32 parts of sulfur,
 four atoms of oxygen or $4 \times 16 = 64$ parts of oxygen,

which added together make 142 parts of sodium sulfate and the molecular weight therefore is 142.0 .

$\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ means a molecule of crystallized sodium sulfate in which there are in addition to the sodium, sulfur, and oxygen, seven molecules of water. This water which forms an essential part of the crystal is called the water of crystallization. The water of crystallization can be driven off by heat and the substance becomes anhydrous.

The formula for ammonium aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, indicates a more complex compound, a molecule of which contains one molecule of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), one molecule of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), and twenty-four molecules of water. Adding these molecules together, the number of individual atoms in this compound are:

2 atoms of aluminum or $2 \times 27.1 = 54.2$ parts of Al
 $3 + 1 = 4$ atoms of sulfur or $4 \times 32 = 128.0$ parts of S
 2 atoms of nitrogen or $2 \times 14 = 28.0$ parts of N
 $(3 \times 4) + 4 + 24 = 40$ atoms of
 oxygen or $40 \times 16 = 640.0$ parts of O
 $(2 \times 4) + (24 \times 2) = 56$ atoms
 of hydrogen or $56 \times 1 = 56.0$ parts of H

making altogether 906.2 parts of

crystallized ammonium aluminum sulfate, having the molecular weight of 906.2 .

Types of Formulas.—The formula for this compound may also be written $\text{Al}_2\text{S}_4\text{N}_2\text{O}_{40}\text{H}_{56}$. Such a formula is called an empirical formula for only the number and kind of atoms are given. From such a formula the quantitative composition of the substance can be calculated, but it does not indicate the way in which the atoms are arranged in the molecule. The arrangement of the atoms, that is, the way in which they group themselves, is shown by the rational formula. The rational formula given above for ammonium alum shows that sulfur is present in the sulfate radical (SO_4), and nitrogen is present in the ammonium radical (NH_4), while some of the oxygen and hydrogen is present as water of crystallization. Thus the rational formula here shows (a) two atoms of aluminum are linked to three sulfate radicals, (b) two ammonium radicals are linked to one sulfate radical, and (c) the crystals contain twenty-four molecules of water.

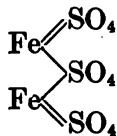
There are four types of formulas: The empirical, the rational, the constitutional and the structural or graphical. The characteristics of each type are as follows:

Empirical Formula.—The empirical formula shows only the number and kind of atoms from which (to repeat) the molecular weight and the percentage composition can be calculated. Thus $\text{F}_2\text{S}_3\text{O}_{12}$ simply means a molecule containing two atoms of iron, three atoms of sulfur, and twelve atoms of oxygen, the molecular weight being $(2 \times 55.9) + (3 \times 32) + (12 \times 16) = 399.8$. Such a type of formula gives nothing further regarding the chemical nature and is practically never used in inorganic chemistry, they are used, however, in organic chemistry for compounds of which only the percentage composition is known, and which have not been fully investigated.

Rational Formula.—The rational formula shows not only the number and kind of atoms, *but also* indicates the way in which the atoms are linked together. Thus $\text{Fe}_2(\text{SO}_4)_3$ means that two atoms of iron are linked to three sulfate radicals, each sulfate radical containing one atom of sulfur and four atoms of oxygen. Such a formula gives some information regarding the chemical characteristics of the compound, *e.g.* this compound would give the characteristic sulfate reaction (a precipitate with barium chloride solution), etc.

Constitutional Formula.—The constitutional formula is a notation which throws further light upon the in-

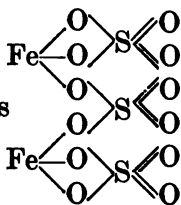
tramolecular arrangement of the atoms. Thus



illustrates the valency bonds and shows that two trivalent iron atoms are linked to three bivalent SO_4 groups, in other words it shows that the iron in this compound has three bonds, and that the sulfate radical has two bonds.

Structural Formula.—The structural formula is the most highly developed form of notation and illustrates the linkage of each individual atom, every bond being represented

by a line. Thus



indicates that the iron is not directly linked to the sulfur atom, as may be assumed from the constitutional formula, but is connected by an oxygen atom to the sulfur. It also shows that there are six single bonds between two iron and six oxygen atoms, likewise six single bonds between three sulfur

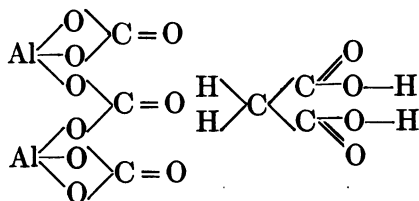
and six oxygen atoms, and finally six double bonds between three sulfur and six oxygen atoms. In a structural formula the radicals are resolved into their simplest components—single atoms, and the connection between each atom is shown. Thus the above structure formula indicates that oxygen is always bivalent, as it has two bonds, while the sulfur is hexavalent having six bonds.

In inorganic chemistry the rational formula is generally used, while the constitutional and structural formulas together with the empirical formula are mainly employed in organic chemistry. In organic chemistry the structure theory has yielded the most magnificent results, for without the recognition of a structure, none of the synthetic substances could be manufactured such as indigo, camphor, dyestuffs, and pharmaceuticals. A modern simplification of structure formulas for organic compounds has been devised in the form of structure symbols (see Canadian Chemical Journal, vol. 2, p. 135, 1918; Science, vol. 48, p. 333, 1918; Chem. News, vol. 118, p. 289, 1919).

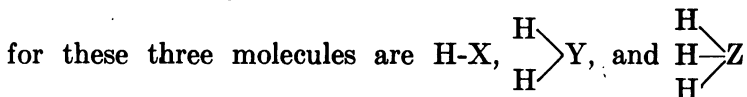
Summary.—Summarized, the four types of formula are:

Empirical:	$\text{Al}_2\text{C}_3\text{O}_9$	$\text{C}_3\text{H}_4\text{O}_4$
Rational:	$\text{Al}_2(\text{CO}_3)_3$	$\text{CH}_2(\text{CO}_2\text{H})_2$
Constitutional:	$\begin{array}{c} \text{Al}=\text{CO}_3 \\ \diagdown \quad \diagup \\ \text{CO}_3 \\ \diagup \quad \diagdown \\ \text{Al}=\text{CO}_3 \end{array}$	$\text{CH}_2 \begin{array}{l} \diagup \text{COOH} \\ \diagdown \text{COOH} \end{array}$

Structural or graphic:



Valency.—What is a bond or valency? How is it possible to depict graphically the intramolecular arrangement of the atoms? Logically we reason that the number of atoms in a molecule must depend upon the force which holds the atoms together; furthermore we find that certain groups of atoms, such as the sulfate radical, are very stable and pass through a number of chemical changes as units, and in such cases the force holding the atoms together must be especially strong. At present we have no means of measuring this force nor do we know its mechanism. However, one of its manifestations is that property of the element which is termed valency. Valency is sometimes defined as the combining power of an atom in regard to hydrogen, but it is more exact to define valency as the combining capacity of an atom or group of atoms (radicals) using an atom of hydrogen as a unit of comparison. Hence if an atom of element X combines with one atom of H and forms a compound HX, then X is said to have a valency of one. If the atom of element Y can combine with two atoms of hydrogen to form a compound of the type H_2Y , then the valency of Y is two, and likewise if an atom of element Z combines with three atoms of hydrogen to give a molecule of the type H_3Z , then Z has a valency of three. The structural formulas



in which each valency is shown by a line. In a compound the atoms which have a valency of one are called monovalent (*e.g.* H, Na, K, Cl, etc.), of two = bivalent (*e.g.* O, Ca, Ba, etc.), of three = trivalent (*e.g.* Al), of four = tetravalent (*e.g.* C, Si, etc.), of five =

pentavalent, of six = hexavalent, of seven = heptavalent, and of eight = octovalent.

Valence Number.—It has become necessary to divide the elements into negative and positive groups (see Chapter 5) and accordingly in each compound there is a negative and positive constituent. This assumption leads to the consideration of positive and negative *valence numbers* (also called *polar numbers*). The basis for the assignment of valence numbers is hydrogen with a positive valence number of one or $+1$.¹ In all stable compounds the sum of the valence numbers must equal zero and by considering H always as $+1$ the positive or negative character of the other elements can be established. Thus in HX the atom X must have a valence number of -1 , in H_2Y the atom Y has a valence number of -2 , in H_3Z the atom Z has a valence number of -3 . Therefore it follows that Cl, in HCl, must have a valence number of -1 , that O, in H_2O , has a valence number of -2 , and N, in NH_3 , has a valence number of -3 .

In some cases elements do not combine with hydrogen, but replace hydrogen (see displacement series), because they are more positive than hydrogen, and accordingly have a positive valence number. Thus Na, which replaces one atom of H, has a valence number of $+1$; calcium replaces two atoms of hydrogen and has a valency of two and valence number of $+2$. The positive valence numbers range from $+1$ to $+8$, while the negative valence numbers range from -1 to -4 . The elements in their free state (uncombined) are assumed to have a valence number of 0.

Univalent and Polyvalent.—However, it is a common misapprehension to assume that a given element can

¹ Only in a very few cases has H a valence number of -1 , such compounds are the hydrides, e.g. NaH, LiH.

form only one type of compound, that is can have only one definite valency or valence number for in many cases an element can form two or more series of compounds, that is, have two or more definite valencies or valence numbers. The first class of elements are spoken of as univalent elements (which must not be confused with monovalent elements), while the second class of elements are called polyvalent elements. In general the alkali metals (Na, K, etc.), earthalkali metals (Ca, Ba, etc.), and earth metals (Al, etc.) are univalent, while the non metals and heavy metals are polyvalent.

A univalent element may consist of monovalent atoms (*e.g.* Na), bivalent atoms (*e.g.* Ca), trivalent atoms (*e.g.* Al), and so on. A polyvalent element may consist of mono- and bivalent atoms (Cu), mono- and trivalent atoms (Au), bi- and trivalent atoms (Fe), bi-, tri- and hexavalent atoms (Cr), mono-, tri-, penta-, and hexavalent atoms (Cl), and so on.

Series of Compounds.—A polyvalent element, that is, an element having two or more valencies, will form two or more series of compounds and these series of compounds will have distinct properties and different names. Thus iron has three series of compounds, namely *ferrous* compounds such as FeCl_2 , FeO , etc. in which the valency is two and the valence number +2; *ferric* compounds such as FeCl_3 , Fe_2O_3 , etc. in which the valency of iron is three and the valence number +3; and finally the *ferrates* such as Na_2FeO_4 in which the valency of iron is six and the valence number +6. Chlorine has four series of compounds: the *chlorides* (NaCl , BaCl_2 , etc.) in which chlorine has a valency of one and a valence number of -1; the *chlorites* (NaOCl , $\text{Ca}(\text{OCl})_2$) in which chlorine has a valency of three, and a valence number of +3; the *chlorates* (KClO_3)

with a valency of five and valence number $+5$; and finally the *perchlorates* (KClO_4) with a valency of seven and valence number of $+7$. Though chlorine is a negative element, like all non metals, it has in only one series of compounds, the chlorides, a negative valence number, and in the other three series a positive valence number. This positive character of the valence number for a negative element is caused by assuming the valence number of oxygen in a compound to be always -2 . This conception aids in understanding oxidation and reduction, as explained further on.

Finding the Valence Number.—From the formula of a compound the valence number of the atoms and their positive or negative character can readily be found by remembering that hydrogen in a compound is always $+1$, and oxygen in a compound is always -2 , and that the sum of the valence numbers in a saturated and stable compound must always be zero. Thus, in water (H_2O) there is $\text{H}_2 = 2 \times (+1) = +2$, and $\text{O} = -2$, therefore $(+2) + (-2) = 0$. In lime (CaO) oxygen is -2 , so calcium must be $+2$. In ferric oxide (Fe_2O_3) there are three oxygen atoms, that is $3(-2) = (-6)$, so the two iron atoms must be $+6$, and one iron atom $+3$, and the valence number of iron in that compound is $+3$. In a similar way the valence numbers for all other atoms are determined and can readily be found by the difference necessary to make the sum zero, hence it is simply an arithmetical problem. A few examples will illustrate this.

Potassium permanganate has the formula KMnO_4 . To find the valence number for the Mn atom add the valence number of K $(+1)$ to the sum of the valence numbers of oxygen $4(-2) = -8$ and get -7 , thus Mn must have $+7$. To make this clearer write the known

valence numbers under the symbols and form an arithmetical equation thus:

$$\begin{array}{ccc} \text{K} & \text{Mn} & \text{O}_4 \\ (+1) + x + 4(-2) = 0 \text{ and hence } x = +7. \end{array}$$

The valence number of nitrogen in sodium nitrate is



$(+1) + x + 3(-2) = 0$. In this case $x = +5$, thus the valence number of nitrogen is +5. Likewise the valence number of chromium in potassium bichromate

is found: $\text{K}_2 \quad \text{Cr}_2 \quad \text{O}_7$

$2(+1) + 2x + 7(-2) = 0$, from this follows that $2x = 12$ and the valence number of one chromium atom is +6.

Oxidation and Reduction.—If an element has several valence numbers, that is, if it forms several series of compounds, we speak of different stages of oxidation. As a rule *oxidation* can be defined as the increase or augmentation of the valence number, that is, a change from a lower to a higher valence number; while *reduction* is the decrease or diminution of the valence number, that is, the change from a higher to a lower valence number. The transformation of ferrous compounds (+2) into ferric compounds (+3) is thus oxidation, while the transformation of a ferrous compound (+2) into metallic iron (0) is reduction. In the former the ferrous compound has been oxidized, in the latter it has been reduced. Again if a chloride (−1) is transformed into chlorine gas (0), the valence number has been increased and the chlorine atom in the chloride is oxidized to free chlorine. If chlorine gas (0) is further oxidized to a chlorite (+3), chlorate (+5), or perchlorate

(+7), the valence number is further increased and therefore the chlorine atom further oxidized. Reduction is a change in the opposite direction, *e.g.* the chlorine atom in a perchlorate (+7) can be reduced to chlorate, chlorite, chlorine, or chloride. Schematically the case is illustrated by the following:

Valence numbers:	-1	0	+3	+5	+7
Type of compounds:	chlorides	chlorine	chlorites	chlorates	perchlorates
Formula:	XCl	Cl ₂	XClO ₂	XClO ₃	XClO ₄
	$\xrightarrow{\hspace{1.5cm}}$ OXIDATION $\xrightarrow{\hspace{1.5cm}}$ $\xleftarrow{\hspace{1.5cm}}$ REDUCTION $\xleftarrow{\hspace{1.5cm}}$				

in which X is a monovalent element.

Any change from left to right is oxidation.

Any change from right to left is reduction.

It is evident from the diagram that the chlorides can not be further reduced, that the perchlorates can not be further oxidized, and that free chlorine gas can be either reduced to chlorides, or oxidized to chlorites, chlorates, or perchlorates.

Similarly there are several series of sulfur compounds:

Valence numbers:	-2	0	+4	+6
Types of compounds:	sulfides	sulfur	sulfites	sulfates
Formula:	X ₂ S	S	X ₂ SO ₃	X ₂ SO ₄
	$\xrightarrow{\hspace{1.5cm}}$ OXIDATION $\xrightarrow{\hspace{1.5cm}}$ $\xleftarrow{\hspace{1.5cm}}$ REDUCTION $\xleftarrow{\hspace{1.5cm}}$			

The conclusions drawn from this diagram are:

Sulfides can be oxidized to free sulfur, sulfites, or sulfates.

Sulfates can be reduced to sulfites, free sulfur, or sulfides.

Free *sulfur* can be oxidized to sulfites and sulfates, or reduced to sulfides.

Sulfites can be oxidized to sulfates, and reduced to free sulfur and sulfides.

Sulfides cannot be reduced, and *sulfates* cannot be oxidized.

It is advantageous for the student to construct such tables and diagrams for other elements which have several series of compounds, such as N, Br, As, P, Fe, Cr, Mn, etc., or to devise a single table in which the more common elements are arranged in the order of their compounds.

Nomenclature.—The different types or series of compounds of an element have different names. These names are formed by the addition of the suffixes -ides, -ites, -ates to a negative element, and -ous or -ic to a positive element.

Endings of Names.—Thus there are for negative elements or radicals the suffixes:

-ides for the lowest form of oxidation, characterized by the absence of oxygen and a negative valence number (nitrides, hydrides, phosphides, carbides, selenides, tellurides, arsenides, etc.).

-ites for the lowest form of oxidation containing few atoms of oxygen, characterized by the lowest positive valence number (nitrites, phosphites, sulfites, arsenites, etc.).

-ates for the normal form of oxidation containing the normal amount of oxygen atoms and characterized by the normal positive valence number (nitrates, sulfates, phosphates, carbonates, arsenates, manganates, chromates, ferrates, etc.).

per- -ates for the highest form of oxidation containing most oxygen atoms and having the highest positive valence number (persulfates, permanganates, perchlorates, etc.).

For positive elements the suffixes are:

-ous indicating the lower form of oxidation, that is, the

lower positive valence number (ferrous, arsenous, mercurous, cuprous, nickelous, plumbous, etc.).

-ic indicating the higher form of oxidation, the higher positive valence number (ferric, arsenic, mercuric, cupric, nickelic, plumbic, etc.).

Key to Nomenclature.—A list of the more common elements, ions, and radicals with their valence numbers can be found in the appendix, and this key to the nomenclature of chemical compounds should enable the student to write the correct formula for any compound, or to give the correct name for any formula of inorganic chemistry.

Summary of Information Contained in a Formula.—From any chemical formula there can be deduced:

(a) The kind of elements and the number of atoms which constitute the molecule.

(b) The weight relation of these elements and the molecular weight of the compound.

(c) The percentage of weight of the elements composing the molecule.

(d) The valency of the elements and, therefore, their stage of oxidation.

Whenever the formula refers to a gas or gaseous compound there is, furthermore, expressed by a formula:

(e) The volume relation of the gaseous constituents. According to Avogadro's law there are, under the same pressure and at the same temperature, in the same volume of any gas the same number of molecules, so it follows that in 1 liter of oxygen there are the same number of molecules as in 1 liter of hydrogen, and as in the formation of water, 2 molecules of H_2 react with 1 molecule of O_2 , so 2 liters of H_2 are required to combine with 1 liter of O_2 .

(f) The specific gravity or density of the gas. Density

can be expressed in three ways according to the unit chosen. (1) Density with regard to oxygen = $D_{(O_2)}$ refers to oxygen gas for comparison and its molecular weight $O_2 = 32$ is taken as a unit, hence the molecular weight of any other gas is also its density or $D_{(O_2)} = \text{Mol. Wt.}$ For H_2 the $D_{(O_2)}$ is 2, for N_2 the $D_{(O_2)}$ is 28, etc. (2) Density with regard to hydrogen = $D_{(H_2)}$ refers to the lightest known gas as unity. In this case the molecular weight of the gas must be divided by the molecular weight of hydrogen, that is $D_{(H_2)} = \text{Mol. Wt.}/2$. Hence for O_2 the $D_{(H_2)}$ is 16, for N_2 the $D_{(H_2)}$ is 14. (3) Density in regard to air as unity = $D_{(air)}$. A certain volume filled with 32 grams oxygen will weigh, when filled with air, 28.95 grams, hence if the density of air is taken as unity, the density of oxygen = $D_{(air)}$ is $32/28.95 = 1.1053$ and accordingly the $D_{(air)}$ of all other gases is found by dividing their molecular weight by 28.95, that is $D_{(air)} = \text{Mol. Wt.}/28.95$.

(g) The weight of 1 liter of gas. The volume occupied by a mole (grammolecule) of any gas is 22.4 liters. Thus a mole of H_2 , or 2 grams of hydrogen, will fill 22.4 liters, a mole of oxygen, or 32 grams of oxygen gas,* will also occupy 22.4 liters under standard conditions of pressure and temperature, hence the simple proportion $22.4 : M :: 1 : x$, and $x = M/22.4$ will give the weight of 1 liter of any gas. In the above equation M represents the molecular weight in grams (= mole), and x the weight of 1 liter of gas in grams.

(h) The volume occupied by 1 gram of any gas. In this case the above proportion becomes $M : 22.4 :: 1 : y$, and $y = 22.4/M$, for if M grams will fill 22.4 liters, then 1 gram will occupy $22.4/M$ liters.

Example.—The formula NH_3 for ammonia means:

(a) The molecule consists of one atom of nitrogen and

three atoms of hydrogen making altogether four atoms in the molecule.

(b) The molecular weight is the sum of the atomic weights, thus 14 parts of nitrogen (by weight—not volume) and $3 \times 1 = 3$ parts of hydrogen give 17 parts of ammonia—hence the molecular weight is 17.

(c) The percentage of nitrogen and hydrogen is calculated from the data given in (b), thus in 17 parts ammonia there are 14 parts of nitrogen, then $17 : 14 :: 100 : x$, hence $14 \times 100/17 = x$, and $x = 82.25$ per cent nitrogen, while $17 : 3 :: 100 : y$ and $y = 3 \times 100/17$ gives for y the percentage of hydrogen as 17.75 per cent.

(d) The valence number of H being +1, three atoms of H are thus equal to +3, therefore the valence number of nitrogen must be -3. From the table in the appendix we see that -3 is the lowest stage of oxidation for nitrogen and it is evident that ammonia can not be further reduced, but can be oxidized to free nitrogen, nitrites, or nitrates.

(e) Nitrogen and hydrogen are both gases, therefore one volume of nitrogen gas and three volumes of hydrogen gas will combine and form ammonia.

(f) The specific gravity or density of ammonia (1) compared with $O_2 = 32$ equals the molecular weight which is $D_{(O_2)} = 17$ for ammonia; (2) compared with $H_2 = 1$, it equals $17/2$, that is $D_{(H_2)} = 8.5$; (3) compared with air = 1, it equals $17/28.95$, that is $D_{(air)} = 0.59$. Ammonia is thus a little over half as light as air and oxygen, but 8.5 times as heavy as hydrogen.

(g) If 22.4 liters of ammonia weigh 17 grams, then 1 liter will weigh $17/22.4 = 0.76$ gram.

(h) If 17 grams of ammonia occupy 22.4 liters, then 1 gram will occupy $22.4/17 = 1.31$ liters.

QUESTIONS

1. Define (a) formula, (b) valency, (c) valence number, (d) oxidation, (e) reduction, (f) radicals, (g) monovalent and univalent elements.

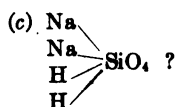
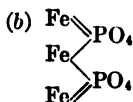
2. Write out all the information contained in the formulas (a) KI, (b) AgNO_3 , (c) H_3PO_4 , (d) K_2HPO_4 , (e) $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$.

3. Write out all the information contained in the formulas for the following gaseous compounds (a) HCl, (b) N_2O_3 , (c) N_2O_5 , (d) CH_4 .

4. Calculate the molecular weights of the following compounds: (a) ferrous sulfate FeSO_4 , (b) ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$, (c) glucose $\text{C}_6\text{H}_{12}\text{O}_6$, (d) sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, (e) bismuth nitrate $\text{Bi}(\text{NO}_3)_3$, (f) potassium alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, (g) nitroglycerin $\text{C}_3\text{H}_5(\text{NO}_3)_3$, (h) hemoglobin $\text{C}_{720}\text{H}_{1171}\text{N}_{144}\text{O}_{313}\text{S}_8$.

5. Calculate the percentage composition of (a) mercuric chloride HgCl_2 , (b) mercurous chloride Hg_2Cl_2 , (c) manganese dioxide MnO_2 , (d) copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, (e) sodium carbonate Na_2CO_3 , (f) crystallized sodium carbonate $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, (g) sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, (h) ammonium nitrate NH_4NO_3 , (i) ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, (j) silver chloride AgCl , (k) silver acetate $\text{AgC}_2\text{H}_3\text{O}_2 \cdot \text{NB}$. In (d) and (f) calculate the percentage of water, not hydrogen and oxygen.

6. What is the rational formula for such a compound as



7. What is the structural formula for the compounds given in 6?

8. Determine the valence numbers of the following elements:

(a) sulfur in H_2S , Na_2SO_3 , Na_2SO_4 , FeS , Na_2S , FeSO_4 , CaS , CaSO_4 , SO_2 , SO_3 , H_2SO_4 ; (b) nitrogen in NH_3 , NH_4OH , N_2O_3 , N_2O , N_2O_5 , NO , NO_2 , HNO_3 , HNO_2 , NH_4Cl , KNO_3 , NH_4NO_3 ; (c) iron in FeO , FeCl_3 , $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, FeCNS , $\text{Fe}(\text{CN})_2$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_2\text{Fe}(\text{CN})_4$. NOTE. The cyan radical (CN^-) has a valence number of -1 like Cl^- ; in it we assume C with -4 , and N with $+3$.

9. Give an example of the lowest and highest stage of oxidation of (a) sulfur, (b) chlorine, (c) nitrogen, (d) manganese, (e) iron, (f) chromium, (g) mercury, (h) copper, (i) lead.

10. Write four or more formulas of different compounds for each series of compounds or stages of oxidation of (a) sulfur, (b) chlorine, (c) iron, (d) nitrogen, and give the proper names to these compounds.

11. Write out the rational formulas for the following compounds:

(a) arsenous chloride, (c) arsenic chloride, (b) cerous nitrate, (d) ceric sulfate, (e) potassium manganate, (f) sodium permanganate, (g) calcium chloride, (h) calcium chlorite, (i) calcium chlorate, (j) potassium per-

chlorate, (*k*) mercuric bromate, (*l*) mercurous arsenate, (*m*) mercuric arsenite, (*n*) ferrous bromide, (*o*) ferric bromide, (*p*) ferrous bromate, (*q*) ferric bromate, (*r*) potassium stannate, (*s*) sodium stannite, (*t*) lithium plumbite, (*u*) potassium plumbate, (*v*) niccolous carbonate, (*w*) niccolic carbonate, (*x*) plumbic bichromate, (*y*) plumbous chromate, (*z*) plumbic chromate. NOTE. Consult the key to nomenclature in the appendix.

12. Which of the following ores contains the highest percentage of iron: (a) hematite Fe_2O_3 , (b) magnetite Fe_3O_4 , (c) limonite $(\text{Fe}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, (d) siderite FeCO_3 , (e) pyrite FeS_2 ?

13. Calculate the percentages of carbon and hydrogen in the first five members of the methane series of hydrocarbons which have the general formula $\text{C}_n\text{H}_{2n+2}$. (In this case the value of *n* is 1, 2, 3, 4, 5.)

14. How many molecules of water of crystallization were present in the crystallized salts when (a) 10 grams of cryst. Na_2CO_3 lose 6.29 grams of water by heating, (b) 10 grams of cryst. BaCl_2 leave after heating a residue of 4.26 grams anhydrous salt, (c) crystallized ZnSO_4 loses after heating 43.8 per cent of its weight?

15. Give the name and formula of a compound composed of (a) 21.60 per cent sodium, 33.33 per cent chlorine, 45.07 per cent oxygen; (b) 70.13 per cent silver, 20.77 per cent oxygen, 9.10 per cent nitrogen; (c) 77.52 per cent lead, 4.49 per cent carbon, 17.88 per cent oxygen.

16. Ten grams of the chloride of a univalent element *x* contain 60.6 per cent of chlorine. If the atomic weight of chlorine is 35.5 what is the atomic weight of the element *x*, and what is its name?

17. Find the anhydrides of the following substances by subtraction of H_2O (a) HNO_3 , (b) H_2SO_4 , (c) HClO_3 , (d) H_3PO_4 , (e) $\text{Cu}(\text{OH})_2$, (f) $\text{Al}(\text{OH})_3$, (g) LiOH , (h) H_4SiO_4 , (i) $\text{Fe}(\text{OH})_3$, (j) HPO_3 . Classify these anhydrides as basic and acid anhydrides.

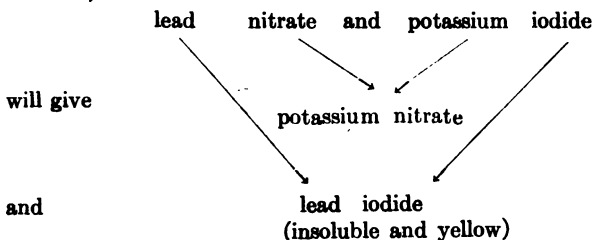
18. 1.251 grams of the oxide of a bivalent element when reduced gave 1.00 gram of a fine metallic powder. What is the atomic weight of the metal, and what is its name?

19. Calculate the simplest formula of the following compounds: (a) 44.07 per cent mercury, 55.93 per cent iodine; (b) 40 per cent calcium, 12 per cent carbon, 48 per cent oxygen; (c) 1.59 per cent hydrogen, 22.22 per cent nitrogen, 76.16 per cent oxygen.

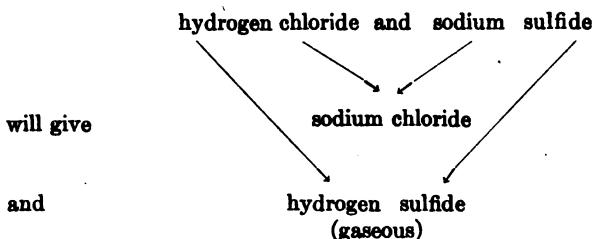
CHAPTER III

EQUATIONS INVOLVING NO OXIDATION OR REDUCTION

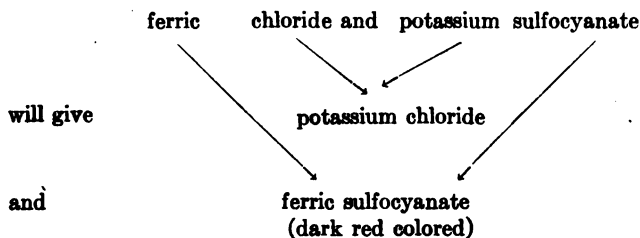
Equations are the sentences of chemistry as they express chemical changes which take place. A chemical change or chemical reaction is a molecular phenomena in which the composition of the molecule is altered. Usually a chemical reaction is brought about by mixing solutions of two different substances. The evidence that a reaction has taken place is (a) the formation of a precipitate (insoluble substance), (b) the formation of gas bubbles (gaseous substance), or (c) the change or formation of a color (differently colored substance). For example, (a) by mixing a solution of potassium iodide and lead nitrate a yellow precipitate is produced, for the following reaction has taken place:



If (b) hydrochloric acid (hydrogen chloride) is added to a solution of sodium sulfide gas bubbles will be observed, for the following exchange has taken place:



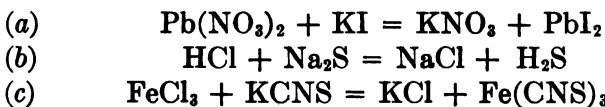
If (c) a few drops of ferric chloride are added to a solution of potassium sulfocyanate an intensely red color will be produced, due to the formation of ferric sulfocyanate:



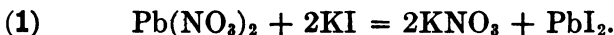
In all three cases, as may be seen, one part of each molecule has changed places with the part of a different molecule. In order to write chemical equations for these reactions the formulas for the substances which act upon each other are placed to the left and connected by the addition sign (+), while the reaction products are written to the right separated by the sign of equality (=), which means that the number and kind of atoms on both sides of an equation must be equal. Thus an equation demonstrates the principle that nothing is lost or gained in the course of transformation, and implies that the molecules to the left are converted into those to the right. In reading an equation the plus sign is rendered by *and*, and the equality sign by *give*. Balanc-

ing of an equation means simply a balancing of the number of atoms, as both sides must be equal.

The formulas of the compounds for the above three reactions are:



None of these equations are balanced. In (a) there are two (NO₃) radicals to the left, while only one appears at the right, and only one I atom at the left, to two I on the right. To balance this double the number of KI on the left, and KNO₃ on the right, and the correct equation will be



In (b) there are two sodium atoms at the left but only one at the right, and if we write 2NaCl at the right, this will necessitate 2 chlorine atoms at the left, that is 2HCl, the correct equation is then:

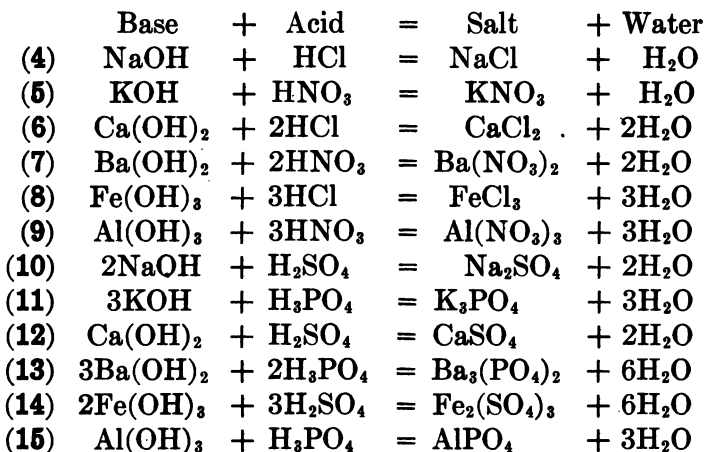


In (c) there are three chlorine atoms in FeCl₃ to the left, while to the right there is only one chlorine atom in KCl, hence writing "3KCl" to the right balances the chlorine atoms but gives three potassium atoms to the right, and as only one potassium atom is at the left, write 3KCNS at the left side and the balanced equation is:

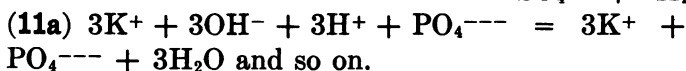
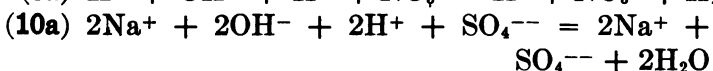
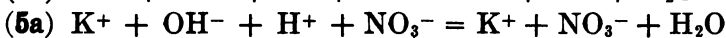
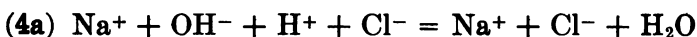


These are now balanced molecular or non-ionic equations, in which no consideration has been given

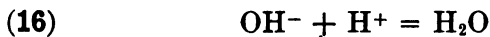
to ionization. The number and kind of atoms are identical on each side of the equality sign. In balancing equations the correct formula for each compound involved is of fundamental importance, for the first step is always to write the formulas of all the compounds, as in (a), (b) and (c). Knowledge of the correct formula naturally requires due consideration of the valency of the elements and radicals concerned. The valency of the common elements must be memorized, and the valency of the radicals can be deduced from the familiar formulas of a few acids and bases. Thus a knowledge of the common acids and bases is essential for the derivation of the formulas of the salts. This derivation is demonstrated in the following equations:



All these equations illustrate that a *base* and an *acid* will give a *salt* and *water*. This type of reaction is called *neutralization*. The equations above are given in the molecular or non-ionic form, in the ionic form they become:



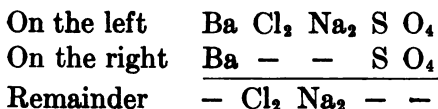
An examination of the ionic equations (4a), (5a), (10a), (11a) shows that some ions have not changed. *E.g.* in (4a) the Na^+ and Cl^- on the left appear also on the right, and therefore have undergone no change. Similarly the K^+ and NO_3^- of equation (5a) remain unchanged. The purpose of an equation is to show a chemical reaction, that is any chemical *change*, and if all the ions which have *not* changed are cancelled, there remains from the above equations



This is the *general equation* for neutralization, and defines neutralization as the combination of one hydroxyl ion with one hydrogen ion to give one molecule of water. By using this universal statement all the particular cases can readily be found by adding to the negative hydroxyl ion (OH^-) the positive metal of any base, and to the positive hydrogen ion (H^+) the negative non-metal or radical of any acid. From the proportion 1 : 1 it is evident that any monoacid base requires one, a diacid base = two, a triacid base = three hydrogen ions; while a monobasic acid requires one, a dibasic acid = two, a tribasic acid = three hydroxyl ions. Thus in equation (10) two molecules of a monoacid base are needed for neutralization of one molecule of a dibasic acid.

If only one of the reaction products is known in a reaction the other reaction product is found by sub-

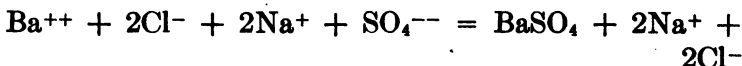
tracting the atoms of the right from those on the left. Thus, if the unfinished equation is $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 = \text{BaSO}_4 + ?$, the following scheme will give the unknown reaction product:



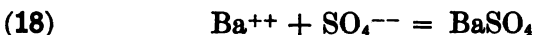
These remaining two chlorine and two sodium atoms naturally give two molecules of sodium chloride, hence the completed equation is



Writing this equation in the ionic form:



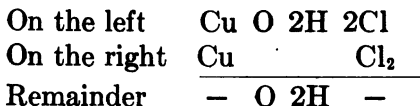
and cancelling those ions which remain unchanged (Cl^- and Na^+) the equation becomes:



This is again a general statement, namely that every soluble barium salt (furnishing the barium ion) with any soluble sulfate (which furnished the sulfate ion) will give a precipitate of barium sulfate (which is insoluble). It is evident that an ionic equation covers many cases, for one may take as the soluble barium salt either BaCl_2 , $\text{Ba}(\text{NO}_3)_2$, etc., and for the soluble sulfate either Na_2SO_4 , K_2SO_4 , etc., but it refers only to one specific reaction, *e.g.*, the formation of barium sulfate. A non-ionic or molecular equation covers only one particular case, for from such an equation as (17) we can not make the deductions which were possible from (18).

Balancing Molecular Equations.—An unfinished equation may be given in which there are more atoms in the

reaction product than in the reacting substances. A simple case is $\text{CuO} + \text{HCl} = \text{CuCl}_2 + ?$, and as 2Cl can not be subtracted from 1 Cl, the number of HCl must be doubled:



which will form one molecule of water, thus:



The problem becomes more difficult when two or more compounds are formed, and in this case greater knowledge of chemistry is required. For example an experiment shows that, on adding a solution of sodium carbonate to a solution of aluminum sulfate, a white precipitate as well as gas bubbles are formed. Hence the reaction products are (a) an insoluble compound, and (b) a gaseous compound. As neither the Al, the Na, nor the SO_4 radical form gaseous compounds, but as the carbonates yield readily CO_2 , the unknown gas must be CO_2 and the unfinished equation is

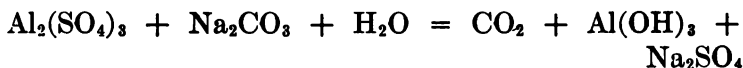


The white precipitate, which is the insoluble compound formed in this reaction, must be a compound of aluminum for all sodium compounds are soluble. At first it appears to be the carbonate, but as carbonic acid is given off, this can not be the case. The other possible compounds to consider would be the oxide and the hydroxide of aluminum, for in this reaction the other insoluble aluminum compounds like the phosphates, silicates, etc. can not be regarded as possible reaction products, as neither of these acid radicals are present. The reaction occurred in

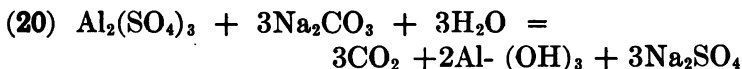
watery solution hence the hydroxide is probably formed; if so, then water must have taken part in the reaction, and the unfinished equation becomes:



The next metal to account for in this equation is sodium, which loses the carbonate radical, and must combine with the sulfate radical to form sodium sulfate:



An examination of this unbalanced equation shows that there are two aluminum to the left and hence $2\text{Al}(\text{OH})_3$ must be formed. There are 3SO_4 —radicals to the left, thus $3\text{Na}_2\text{SO}_4$ are produced,—this in turn requires $3\text{Na}_2\text{CO}_3$, and these three molecules will yield 3CO_2 . Finally as $2\text{Al}(\text{OH})_3$ are formed, there are $2 \times 3 = 6$ hydrogen atoms necessary and these are present in $3\text{H}_2\text{O}$. Making these corrections, the finished and balanced equation is:

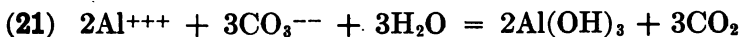


As a test of correctness the following checking scheme is used:

	Al	(SO ₄)	Na	C	O	H
To the left	2	3	6	3	9+3	6
To the right	2	3	6	3	6+6	6

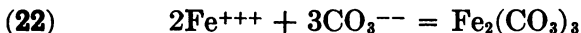
From this we see that one atom of oxygen from each of the three carbonate radicals reappears in a molecule of the hydroxide.

To write equation (20) in the ionic form the soluble salts are written as ions, while those ions which appear on both sides are cancelled, and there remains:

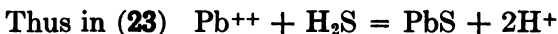


The general rule drawn from this equation is that every soluble aluminum salt will react with soluble carbonates and water to give insoluble aluminum hydroxide and gaseous carbon dioxide. It is again evident that equation (20) referred to a particular case, while equation (21) refers to a specific reaction which covers a number of particular cases, for the aluminum sulfate may be substituted by aluminum chloride, or aluminum nitrate, etc., and the sodium carbonate by potassium carbonate, or lithium carbonate, etc.

Balancing Ionic Equations.—In balancing an unfinished ionic equation the charges on the ions must also be balanced. As a rule the balancing is simple if the charges are *balanced first*, before the atoms are balanced. Thus in $\text{Fe}^{+++} + \text{CO}_3^{--} = ?$; there are three positive charges on the iron, and two negative charges on the carbonate radical, and to make their sum zero converse and add $2(+3)$ and $3(-2)$, that is two ferric ions (together six positive charges) and three carbonate ions (together six negative charges), therefore:



It is not necessary that the sum of the charges on each side of an equation be zero, as in (22), it can be any integer, *provided* this sum is the same on both sides of the equation.



there are two positive charges on the left which equal the two positive charges on the right. Similarly in the equation



there is on both sides of the equations an excess of two negative charges, while in



the sum is four negative charges on both sides. The sum of the ionic charges may thus be different for different reactions, but must be equal on both sides of the equation.

The general meaning of the last four ionic equations is that:

- (22) any soluble ferric salt with any soluble carbonate will form an insoluble precipitate of ferric carbonate;
- (23) any soluble lead salt and hydrogen sulfide will give insoluble lead sulfide and liberate hydrogen ions;
- (24) zinc hydroxide dissolves in bases (OH^-) and forms zincates and water;
- (25) soluble bichromates with bases give soluble chromates.

Rules for Finishing and Balancing Equations.—The rules in balancing and finishing equations are summarized as follows:

(A) Unfinished equations in which only the reacting substances are given, and none or one of the reaction products (compare equations (17), (18), (19), (20)). In such cases there is usually an exchange of the positive atoms or radicals, according to the type $\text{MN} + \text{M}'\text{N}' = \text{M}'\text{N} + \text{MN}'$, where M and M' are positive elements, and N and N' negative elements or radicals. The finishing of such problems requires:

First, the correct formulas for the reacting substances, (to the left) and the correct formulas of the reaction products (to the right). The reaction products are usually gotten by exchanging the positive or the negative constituents of the molecules, giving due consideration to the valency.

Second, balance the atoms, as given under B.

(B) Balancing equations means equalizing the number and kind of atoms on both sides of the equation: Begin with any symbol on the left and check the same number

of symbols on the right—if the number is unequal, select the highest number on either side of the equation, and write the same number before the formula containing the symbol on the opposite side of the equation. Hydrogen and oxygen atoms are often balanced by writing H_2O on the opposite side of the equation.

(C) Balancing ionic equations requires:

First, equalizing the charges on both sides of the equation: the sum of the charges on the left must equal the sum of the charges on the right. If the sums are unequal and they cannot be made equal in the way shown for equation (22), the addition of H^+ or OH^- is necessary, depending upon whether the reaction occurs in acid or alkaline solution.

Second, balance the atoms, as given under B.

An ionic equation is always a general statement of the chemical properties of an ion, while the non-ionic or molecular equation is a particular statement of a definite case, or of the weight relations in a certain reaction, for by introducing the respective mass of the atoms and molecules, the proportions of weight of the reacting substances are found. The following questions involve some of these weight relations and with the aid of the tables in the appendix should offer no difficulty.

QUESTIONS

1. Define (a) equation, (b) ionic equation, (c) neutralization.
2. What is the cost of materials for preparing 100 kg. of 30 per cent solution of HCl from NaCl and H_2SO_4 , if the kg. of NaCl costs 5¢, and the kg H_2SO_4 , 6¢?
3. How many grams of KBr and AgNO_3 are needed to make half a kg. of AgBr ?
4. Eighty grams of a solution of sulphuric acid are sufficient to dissolve 22 grams of cupric oxide. What was the percentage by weight of sulphuric acid in the original solution?
5. Three hundred and ten grams of borax crystals are dissolved in a

little water and concentrated sulphuric acid is added. How many grams of H_2SO_4 should be used, and how many grams of boric acid are obtained?
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 4\text{H}_3\text{BO}_3 + 5\text{H}_2\text{O}$.

6. How many kilograms of KNO_3 can be made from a metric ton of NaNO_3 , and how many kilograms of KCl must be used? (A metric ton equals 1,000 kg.)

7. Calculate the loss in weight if 15 grams of marble are heated until the change is complete.

8. To 32 grams of a solution of sulphuric acid an excess of BaCl_2 was added. The BaSO_4 obtained weighed 11.43 grams. Calculate the percentage of sulphuric acid in the sulphuric acid solution.

9. How many grams of HFl can be made from 20 grams of fluorspar (CaF_2), and how many grams of sulphuric acid must be added? What will be the volume of HFl gas, if one mole occupies 22.4 liters?

10. How many grams of NH_3 can be obtained from 50 grams of ammonium chloride, and how many grams of calcium hydroxide are necessary? What will be the volume of the NH_3 gas?

11. How many grams of nitric acid will be obtained by: (a) heating 250 kg. of sodium nitrate with sulphuric acid; (b) heating 250 kg. of potassium nitrate with sulphuric acid?

12. How many grams of crystallized cupric nitrate (containing 3 mol. H_2O) must be heated to redness to make 50 grams of cupric oxide?

13. How many grams of nitric acid are needed to convert: (a) 500 grams sodium hydroxide into sodium nitrate; (b) 500 grams potassium hydroxide into potassium nitrate; (c) 500 grams calcium hydroxide into calcium nitrate; (d) 500 grams calcium oxide into calcium nitrate; (e) 500 grams barium hydroxide into barium nitrate?

14. A solution contains exactly 40.00 grams of sodium hydroxide in 1 liter. Calculate the quantities by weight of (a) HCl (b) HNO_3 , (c) H_2SO_4 , (d) H_3PO_4 which will be required to neutralize 10 c.c. of this solution.

15. In ascertaining the strength of a dilute solution of HCl , 50 c.c. were measured out and neutralized with a solution of sodium hydroxide, containing 0.003 grams NaOH in 1 c.c. Thirty-five cubic centimeters of this solution was required. What is the strength of the HCl ? How many grams HCl are in 1 c.c.?

16. Forty cubic centimeters of a solution of potassium hydroxide containing 0.01 grams of KOH in 1 c.c. were required to neutralize 40 c.c. of a solution of H_2SO_4 . How many grams of sulphuric acid did 15 c.c. of the sulphuric acid solution contain?

17. Three hundred and eighty grams of mercuric chloride are dissolved in water. How many grams of KI must be added to precipitate all the mercury? How many grams of HgI_2 will be obtained?

18. If 5 grams of crystallized copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are dissolved

in water, how many grams of H_2S are necessary to precipitate all the copper as copper sulfide? How many grams of FeS and 25 per cent HCl are required to generate enough H_2S for this purpose?

19. How would you make a normal solution of the following substances: (a) HCl , (b) HNO_3 , (c) H_2SO_4 , (d) NaOH , (e) NH_4OH ? How would you make a N/10 solution of (f) $\text{Ca}(\text{OH})_2$, (g) NaCl , (h) SO_2 ; a 2N solution of (i) HFl , (j) H_3PO_4 , (k) FeSO_4 ?

20. Answer the following problems by inspection:

(a) How much KOH will be required to neutralize 1 liter N solution of HNO_3 , 1 liter N solution of H_2SO_4 , 1 liter N solution of H_3PO_4 ? (b) How many grams of $\text{Ca}(\text{OH})_2$?

21. Write the equations for preparation of the following:

- Cupric oxide from cupric carbonate;
- Cupric chloride from cupric oxide;
- Ferric hydroxide from ferric sulphate;
- Ferrous sulfide from ferrous sulphate;
- Aluminum carbonate from aluminum nitrate;
- Aluminum hydroxide from aluminum chloride.

State in each case which substances are necessary for the reaction and which substances are precipitated.

22. How would you make the following compounds:

- Cupric chloride from cupric sulfate?
- Cupric sulphate from cupric chloride?
- Ferrous sulphate from ferrous sulfide?
- Ferric chloride from ferric sulphate?
- Aluminum sulfate from aluminum chloride?
- Aluminum chloride from aluminum sulfate?

As none of these compounds are insoluble, in which way should they be prepared? Base your answers on equations which show possible reactions.

23. You are given a quantity of lead acetate solution. How would you prepare: (a) lead chloride, (b) lead nitrate, (c) lead sulfate, (d) lead chromate, (e) lead oxide, (f) lead carbonate from this solution?

24. Starting with lime CaO how would you make (a) CaCl_2 , (b) CaSO_4 , (c) $\text{Ca}(\text{NO}_3)_2$, (d) CaCO_3 , (e) solid $\text{Ca}(\text{OH})_2$?

25. Describe at least three ways of making ferric chloride from ferric sulphate.

26. Write the equations for the formation of: (a) Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ from ferric ions and ferrocyanide ions; and (b) Thurnbull's blue $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ from ferrous ions and ferricyanide ions.

27. Finish the following equations:

- $\text{Zn}^{++} + \text{H}_2\text{S} =$
- $\text{NiCO}_3 + \text{H}_2\text{SO}_4 =$
- $\text{Ni}^{++} + (\text{NH}_4)_2\text{S} =$

- (d) $\text{HgNO}_3 + \text{Cl}^- =$
- (e) $\text{Al}^{+++} + \text{OH}^- =$
- (f) $\text{Al}(\text{OH})_3 = \text{Al}_2\text{O}_3 + ?$
- (g) $\text{FeS} + \text{H}^+ = \text{H}_2\text{S}$
- (h) $\text{CaF}_2 + ? = \text{CaSO}_4 + ?$
- (i) $\text{Ba}^{++} + ? = \text{BaCO}_3 + ?$
- (j) $\text{Al}^{+++} + ? = \text{Al}(\text{OH})_3 + \text{H}^+$
- (k) $\text{Ca}(\text{OH})_2 + ? = \text{Ca}(\text{SH})_2 + \text{H}_2\text{O}$
- (l) $\text{NaCl} + \text{NH}_4\text{HCO}_3 = \text{NaHCO}_3 + ?$
- (m) $\text{CuO} + ? + \text{H}_2\text{O} = \text{Ba}(\text{OH})_2 + \text{CuS}$
- (n) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} = \text{Co}^{++} + ? + ?$
- (o) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} = \text{CoCl}_2 + ?$
- (p) $\text{MnCl}_2 + (\text{NH}_4)_2\text{S} = \text{Mn}(\text{SH})_2 + ?$
- (q) $6\text{KCN} + \text{FeSO}_4 = \text{K}_4\text{Fe}(\text{CN})_6 + ? \text{K}_2\text{SO}_4$

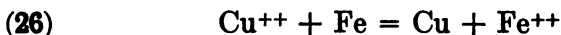
28. Balance the following equations:

- (a) $\text{CaCO}_3 + 2\text{HNO}_3 = \text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2$
- (b) $\text{SiCl}_4 + \text{NH}_3 = \text{Si}(\text{NH}_2)_4 + \text{NH}_4\text{Cl}$
- (c) $\text{SiS}_2 + \text{H}_2\text{O} = 2\text{H}_2\text{S} + \text{SiO}_2$
- (d) $\text{K}_2\text{SiF}_6 + \text{KOH} = \text{KF} + \text{K}_4\text{SiO}_4$
- (e) $\text{SiF}_4 + \text{H}_2\text{O} = \text{H}_4\text{SiO}_4 + \text{H}_2\text{SiF}_6$
- (f) $\text{PCl}_5 + \text{AsF}_3 = \text{PF}_5 + \text{AsCl}_3$

CHAPTER IV

EQUATIONS INVOLVING OXIDATION AND REDUCTION

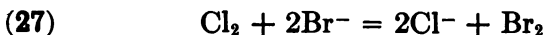
Oxidation and Reduction.—Oxidation and reduction are defined in a previous chapter as the increase or decrease in the valence numbers. In an equation this increase or decrease of the valence number must also be balanced. Thus an increase of two in the valence number of one element must be balanced by a decrease of two in the valence number of some other element. In other words, oxidation cannot take place unless there is a reduction in some other element. In its simplest form this principle is illustrated in the displacement reaction:



In this case the metallic iron (Fe = valence number 0) acquired two positive charges from the cupric ion (Cu^{++} = valence number +2) and was oxidized (increased its valence number) to ferrous ion (Fe^{++} = valence number +2), while at the same time the cupric ion was reduced (decreased its valence number) to metallic copper (Cu = valence number 0). The experiment is readily performed by placing a piece of blank iron in a solution of any copper salt, *e.g.*, blue vitriol, and the iron will be covered by a film of finely divided copper in the form of a brownish precipitate. If sufficient time is given for the reaction to take place all of the copper may be precipitated, and the blue color of the solution will change to the greenish color of the ferrous ion. In this case

the metallic iron has replaced the copper (see also Chapter 5).

Not only with positively charged elements, but also with negatively charged elements such a displacement takes place:



In this case chlorine (0) was reduced to chloride ion (-1), and the bromide ion (-1) was oxidized to bromine (0). It should be noted that in equation (26) the transformation of an element to its ion was oxidation, while in equation (27) this transformation was a reduction, in the first case the valence number increased, in the second case the valence number decreased.

Metals and Non-metals.—As a general rule metals are oxidized, and non-metals are reduced to binary¹ compounds, and oxidized to tertiary² compounds. An exception to this rule is the direct oxidation of non-metals by oxygen, *e.g.*, burning sulfur, phosphorus, or carbon in air, as in these reactions binary compounds are formed, *e.g.* SO_2 , P_2O_5 , CO , or CO_2 . The reason for this is found in the assumption that oxygen is always considered negative, or -2 , and therefore, in non-metal oxides, the non-metal is positive with regard to oxygen; while in non-metal hydrides (*e.g.*, H_2S , NH_3 , CH_4) and the binary salts (*e.g.*, KCl , CaS , AlN , FeC_2) the non-metal is always negative, as hydrogen is positive ($+1$) and all metals are positive.

In the equation



the mercury of mercuric oxide was reduced, the valence

¹ Binary compounds have only two kinds of atoms, *e.g.*, NaCl , FeCl_2 .

² Tertiary compounds have three different kinds of atoms, *e.g.*, KCN , BaSO_4 , Na_3PO_4 .

number being decreased from 2 to 0, while the oxygen of mercuric oxide was oxidized, the valence number being increased from -2 to 0. However, in the equation



metallic sodium (O) is oxidized to sodium oxide ($\text{Na} = +1$), while the oxygen gas (O_2) was reduced to an oxide (-2).

Balancing Oxidation and Reduction.—As seen in these equations, oxidation is exactly counter-balanced by reduction, for the increase in valence number is the reciprocal of the decrease in valence number, in other words, if the increase is added to the decrease the sum is zero. Thus in equation:

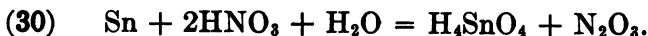
(26) oxidation of iron to ferric ion = increase of two,
reduction of cupric to copper ion = decrease of two;

(27) oxidation of two bromide ions to bromine = increase
of $2 \times 1 = 2$
reduction of chlorine to chloride ions = decrease of
 $2 \times -1 = -2$

(28) oxidation of two oxides to oxygen = increase of
 $2 \times 2 = 4$
reduction of two mercuric to mercury = decrease
of $2 \times 2 = -4$

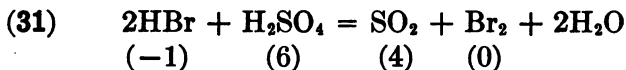
(29) oxydation of four sodium = increase of $4 \times 1 = 4$
reduction of two oxygen to oxide = decrease of
 $2 \times 2 = -4$

Sum Is Zero.—The sum of this increase and decrease is always zero in a correct equation. A more complex example is:

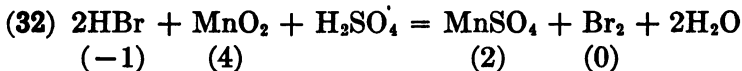


In this equation metallic tin (0) has been oxidized to a stannic compound (4)—stannic acid, while the nitrogen of nitric acid (5) has been reduced to nitrous oxide (3), thus the tin has increased by 4, and two nitrogen atoms have each decreased by 2, and $2(-2) = -4$.

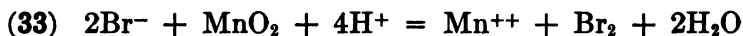
This increase or decrease of the valance number is perhaps best illustrated by writing the valence numbers which change under the respective symbols:



In this reaction two bromine atoms (-1) of hydrobromic acid have been oxidized to free bromine (0), and the sulfur (6) of sulfuric acid has been reduced to sulfur (4) of sulfur dioxide. However in



not the sulfur of sulfuric acid, but the manganese (4) of manganese dioxide has been reduced to manganese (2) of manganous sulfate. Writing the later equation in the ionic form:



illustrates the rule that any soluble bromide in the presence of hydrogen ion (any acid) will give, with manganese dioxide, a manganous compound and free bromine.

In balancing an unfinished equation it is always advantageous, and in many cases absolutely necessary, to strictly follow the rules.

The Three Rules.—*First*, balance the valence numbers of the elements. Write under each symbol its valence number, then observe which elements are oxidized or

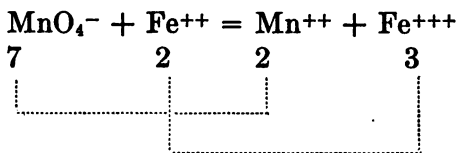
reduced. The oxidation must be the reciprocal of the reduction, for if the element A has been oxidized from 2 to 4, (increased two steps) and the element B has been reduced from 3 to 0, (decreased three steps) then 3 atoms of A will counterbalance 2 atoms of B, for $3 \times 2 = 6$, and $2 \times (-3) = -6$, and $6 + (-6) = 0$.

Second, balance the ionic charges on both sides. Write on each side the sum of the ionic charges of all the ions. This sum may be either +, -, or 0, but must be the same on each side. If the sum is not equal and the reaction occurs in an acid solution, add the required number of hydrogen ions (H^+) to the proper side, and, if it occurs in alkaline solution, add hydroxyl ions (OH^-), until the sum becomes equal.

Third, balance the atoms. Their kind and number must be equal on both sides.

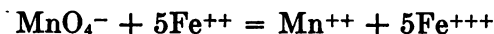
Strict adherence to the sequence of these three steps is essential for a speedy solution of the most complex problems; for any attempt to balance the number of atoms before the valence numbers and ionic charges are balanced may result in failure or an incorrect solution. A few examples will illustrate the method.

Examples.—Problem 1.—Write an equation for the oxidation of a ferrous salt to a ferric salt by potassium permanganate in acid solution. Supposing the permanganate is reduced to a manganous salt, we write the four symbols for the ions and place under each symbol the respective valence numbers:



Connecting the corresponding valence numbers by the

dotted lines shows that manganese has been reduced from 7 to 2 (5 steps), while the iron is oxidized from 2 to 3 (1 step). In order that oxidation and reduction are balanced, the factors are reversed: 1×5 steps = 5×1 step, which means that 1 molecule of permanganate is sufficient to oxidize 5 molecules of a ferrous compound and the unfinished equation becomes:



The proportion of 1Mn to 5Fe must be kept throughout the succeeding operations—it may be doubled (2:10) or tripled (3:10)—but the proportion of 1 to 5 must be preserved.

The second step is balancing the ionic charges. They are counted and added together separately for each side of the equation, thus:

on the left:

one negative charge on the permangante	=	- 1
5 × 2 positive charges on the iron .	=	<u>10</u>
therefore excess of positive charges		9

on the right:

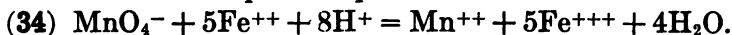
two positive charges on the manganese	=	2
5 × 3 positive charges on the iron	=	<u>15</u>
a total of positive charges		17

As the number of charges on both sides must be equal, for nothing can be gained or lost during a chemical reaction, some other substance must have reacted which furnished either 8 positive charges to the left, or yielded 8 negative charges to the right side of the equation. The positive charges are usually furnished by H^+ (acids), and the negative charges by OH^- (bases), and

as it was specified that the reaction occurred in acid solution, 8H^+ must be added to the left in order to balance the charges:



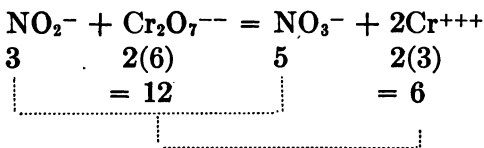
The sum of the ionic charges is thus equal on both sides for $(-1) + 5(2) + 8(1) = (2) + 5(3) = 17$; and the first and second step of balancing is accomplished. It remains to balance the atoms. Checking off the atoms leaves 4 oxygen atoms and 8 hydrogen atoms on the left which will naturally give 4 molecules of water. Therefore the completed equation is



This ionic equation is the general statement of the problem and enables the construction of many equations for particular cases by simply supplying the ions with the corresponding radicals or elements. In other words, the permanganate (MnO_4^-) can be any soluble permanganate, either of sodium, potassium, etc.; the ferrous salt can be any soluble salt, either sulfate, chloride, nitrate, etc.; and the acid can be either HCl , H_2SO_4 , HNO_3 , etc.

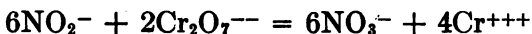
Problem 2.—A nitrite solution is oxidized to a nitrate solution by an acidified bichromate solution:

First, the valence numbers are written under the ions

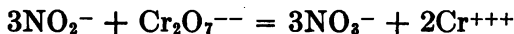


The nitrogen of the nitrite therefore has been oxidized from 3 to 5—increased 2 steps. The chromium of the chromate has been reduced from 12 to 6—decreased 6

steps. To balance the factors are reversed, $6(2) = 2(6)$, therefore,



The proportion 6 : 2 can in this case be simplified to 3 : 1 and the unfinished equation becomes:



Second, the charges are counted on both sides, thus

on the left there are 3 nitrites	= 3 negative charges
1 bichromate	= 2 negative charges
a total of	<u>5 negative charges</u>

on the right there are 3 nitrates	= 3 negative charges
2 chromic ions	= <u>6 positive charges</u>
a total of	<u>3 positive charges</u>

To balance +3 and -5 requires either 8 positive charges to the left, or 8 negative charges to the right. As the reaction occurs in acid solution, eight hydrogen ions must be added which give the necessary eight positive charges to the left side, and the equation becomes:



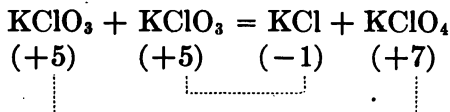
and the sum on both sides equals 3 positive charges:

$$3(-1) + (-2) + 8(1) = 3(-1) + 2(3) = 3$$

Third, the atoms are balanced. Nitrogen and chromium balance. On the left are $(3 \times 2) - 7 = 13$ oxygen atoms, while on the right there are only $(3 \times 3) = 9$. This excess of 4 oxygen atoms at the left will give with the 8 hydrogen atoms four molecules of water and the finished equation becomes:



In a few cases it may happen that a substance is oxidized and reduced in the same reaction, that is, one part of the substance is being oxidized and the other is being reduced. It is then advisable to write the formula of this substance twice:



This diagram shows that the chlorine (+5) of the chlorate is reduced to chloride (-1), while another part of the chlorate is oxidized to perchlorate (7). In the first case the valence number has decreased 6 steps and in the second it has increased 2 steps. It follows, that for every 2 molecules of potassium chlorate giving 2 molecules of potassium chloride, 6 molecules of potassium chlorate are transformed to 6 molecules of potassium perchlorate, hence 8 molecules of potassium chlorate give 2 molecules of potassium chloride and 6 molecules of potassium perchlorate, which can be simplified to



QUESTIONS

1. Define (a) oxidation and reduction, (b) displacement, (c) stages of oxidation, (d) ionic equation, and (e) non-ionic equation.

2. What is the cost of preparing 5 kg. of hydrogen gas from zinc and sulfuric acid? (Assume the price of Zn to be 50¢ per kilogram, and that of H_2SO_4 6¢ per kilogram.)

3. What weight of phosphorus will completely remove the oxygen from 2 kg. of air? (Assume that air contains 23 per cent of oxygen by weight.)

4. How many grams of oxygen can be obtained from 75 grams of a 3 per cent solution of hydrogen peroxide?

5. How many grams of a 6 per cent solution of hydrogen peroxide will convert 5 grams of lead sulfide into lead sulfate?

6. How many grams of potassium chlorate are necessary to furnish

the oxygen for conversion of 25 grams metallic copper into cupric oxide? (b) How many grams of KCl will be formed? (c) Can this reaction be written in the ionic form? (Give reasons.)

7. How many grams of ammonium nitrate are necessary to make 100 grams of nitrous oxide, which is formed by heating the salt?

8. What are the substances formed when a bromine solution is added to a potassium hydroxide solution?

9. Write an equation for the reaction of (a) bromide, manganese dioxide, sulfuric acid to give free bromine; (b) sodium bromide, manganese dioxide, sulfuric acid to give free bromine; (c) potassium bromide, manganese dioxide, phosphoric acid to give bromine.

10. How many grams of 50 per cent sulfuric acid can be made from 10 grams of sulfur by burning the sulfur in air, and passing the sulfur dioxide thus formed over finely divided platinum which acts as catalyser, thus producing sulfur trioxide? (Give complete set of equations.)

11. Twenty kilograms of phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$, are heated with sand, SiO_2 , and coke, C, in an electric furnace. The coke burns to CO, the phosphate is reduced to phosphorus, and CaSiO_3 is formed. How many grams of phosphorus are obtained?

12. Two grams of an alloy of Cu and Ag are dissolved in nitric acid. To this solution HCl is added. The precipitated AgCl weighs 1.8 grams. (a) How many grams of Ag and Cu were present? (b) What is the percentage of Ag and Cu in the alloy?

13. Thirty kilograms of an ore containing 60 per cent Sb_2S_3 are heated with iron. How many kilograms of antimony are formed?

14. A metric ton (= 1000 kg.) of pyrites containing 8 per cent of foreign substances is burned in a sulfuric acid plant. (a) How many kilograms of ferric oxide remain? (b) How many kilograms of sulfur dioxide are formed?

15. How many grams of (a) bromine, (b) iodine are produced by passing a current of chlorine gas through a solution of (a) 25 grams of magnesium bromide, (b) 10 grams of potassium iodide?

16. How many grams of (a) water, (b) carbon dioxide are formed by burning 1 kg. of methane (CH_4)?

17. The hydrogen obtained from 24.2 grams of zinc and hydrochloric acid is passed over heated mercuric oxide. How many grams of water and how many grams of mercury are produced?

18. How many grams of nitric oxide, NO, are formed when 75 grams of copper are dissolved in nitric acid?

19. How many grams of chlorine can be obtained by heating 43.5 grams of manganese dioxide with hydrochloric acid?

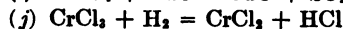
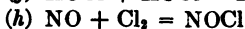
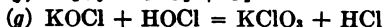
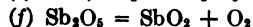
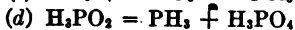
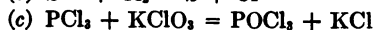
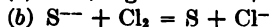
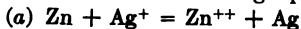
20. How many grams of cryst. copper nitrate must be heated to redness in order to obtain 46.2 grams of NO_2 ? The other products formed in this reaction are O_2 , H_2O , and CuO.

21. How many grams of (a) iron, (b) zinc, (c) aluminum are required to precipitate 10.8 grams of silver from a silver nitrate solution?

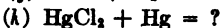
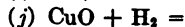
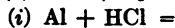
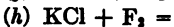
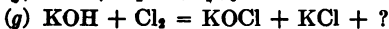
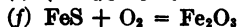
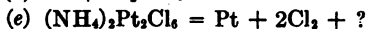
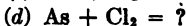
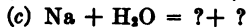
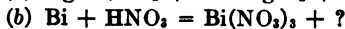
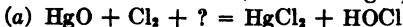
22. How many grams of iodine will be precipitated from a potassium iodide solution by the chlorine, which is formed from 21.75 grams manganese dioxide and hydrochloric acid?

23. How many kilograms of iron and sulfuric acid will be needed to make 100 kg. of hydrogen gas?

24. Balance the following equations:

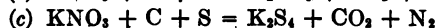
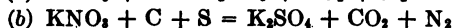


25. Finish and balance the following equations:



26. Ordinary gun powder is a mixture of saltpeter, carbon, and sulfur. The reaction products are K_2CO_3 , K_2SO_4 , K_2S_4 , SO_2 , and N_2 .

Complete the following reactions:



Assuming that these are all the reactions concerned in an explosion, calculate the correct proportion of saltpeter, carbon and sulfur.

27. Construct equations for the reduction of potassium from potassium sulfide by means of (a) iron, (b) aluminum, (c) manganese. The reaction products are (a) FeS , (b) Al_2S_3 , and (c) MgS . Which metal per pound will yield the largest quantity of potassium? Which metal is most economical? (A pound of Fe costs 5¢, Al = 25¢, and Mg = 30¢.) Which reaction will take place most rapidly?

CHAPTER V

CONTROL OF REACTIONS

A chemical reaction is a molecular phenomenon by which the composition of the molecule is changed. The most frequent type of reactions are those in which one part of the molecule is exchanged by a part of a different molecule—thus in the reaction $AB + CD = AD + CB$ we may say that B has changed places with D, or A has been exchanged by B for C, and we draw the inference, that either A has a greater attractive force to D than to B, or that B has a greater attractive force to C than to A. Postponing a discussion of this force of attraction holding the atoms in the molecules together, we find that a reaction is practically never 100 per cent efficient. This means that not all of the AB, and not all of the CD has been transformed to AD and CB. In every reaction there is a certain and definite percentage of transformation, and this percentage forms the basis of the measurements in physical chemistry. However, the percentage of reacting substances and reaction products is not the only factor which can be experimentally determined for a given reaction. Every reaction requires a certain space of time; some may be instantaneous; some may be so extremely slow as to be hardly recognizable. Ionic reactions or reactions which occur in solutions are usually instantaneous, while molecular reactions usually require a measurable period of time. For both kinds of reactions, ionic and molecular, it is essential that the ions or molecules come in close contact, for if the two ions or molecules are far apart, they cannot

react upon each other. The contact of ions or molecules is usually termed ionic or molecular collision. Any physical means which facilitates ionic or molecular collisions will thus increase the possibility of a reaction taking place. The physical means which increase or decrease the possibility of collisions and so influence a chemical reaction may be of a mechanical, thermal, or electrical nature.

Speed of Reaction.—The speed of a reaction is shown in the proportional amount of reaction-products (AD and CB) which are formed from the reacting substances (AB and CD) in a given period of time. Thus it becomes evident that the control of reactions depends entirely upon the regulation of the speed of the reaction. By application of mechanical, thermal, or electrical means, either alone or in combination, the speed of a reaction is either (a) accelerated (made to proceed faster), (b) retarded (made to proceed slower), (c) stopped (made to stand still), or (d) reversed (made to proceed in the opposite direction). Hence for every reaction there are favorable as well as unfavorable conditions.

THE MECHANICAL CONTROL: Surface, Catalyzers, Concentration, and Pressure

Frequency of Collisions is Influenced by Number of Molecules Coming in Contact.—The mechanical means which influence the frequency of molecular collisions are those which regulate the number or the amount of molecules. The more molecules collide with each other, the greater the possibility of a reaction, and *vice versa*. This can be accomplished in four different ways: (1) by increasing the surface of contact between two substances, (2) by mechanical catalyzers, (3) by higher concentration, (4) by greater pressure.

Increase of Surface by Subdivision.—An increase of the contact surface between two substances will naturally increase the number of different molecules coming into close contact, and hence increase the possibility of the molecules colliding. By placing a cube of iron containing 1 c.c. in hydrochloric acid, it is evident that the contact surface between the solid and liquid is 6 sq. cm., for the edges of the cube are each 1 cm. long, and each side has a surface of 1 sq. cm., and there are six sides on the cube. If this cube is cut into eight smaller cubes, as shown in Fig. 1, the volume and mass of the iron, as well

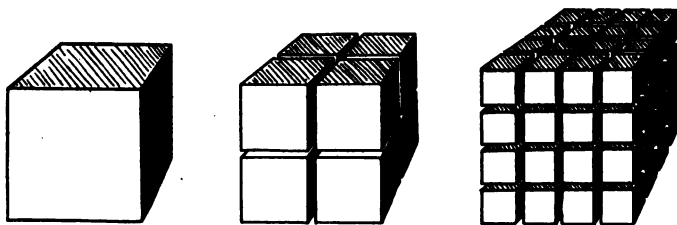


FIG. 1.—Increasing the surface by subdivision.

as the total number of iron molecules has not been changed, but the surface has been doubled, making it 12 sq. cm., and consequently twice as many molecules of iron are in contact with hydrochloric acid. If we divide these cubes again into a total of 64 smaller cubes, the total surface of the same amount of iron will be 23 sq. cm. It is evident that this division can be theoretically continued until we have single iron molecules. It is also evident that the smaller the cubes, the greater the surface, and the greater the contact surface between the solid and the liquid, therefore, the greater the possibility of molecular collisions. It is thus possible to predict that the single large iron cube will dissolve more slowly than the four small ones, and that the 64 smaller ones will dis-

solve faster than the four small ones. The following table will be of interest:

INCREASING THE SURFACE OF A 1-C.C. CUBE BY SUBDIVISION

Edge length (a)	Number of cubes (b)	Total surface (c)	Cubes are	Magnitude (d)
1 cm.	1	6 cm. ²	visible	coarse granules
0.1 cm. = 1 mm.	10 ³	60 cm. ²	visible	fine granules
0.01 cm.	10 ⁴	600 cm. ²	visible	coarse powder
0.001 cm.	10 ⁶	6,000 cm. ²	microscopic	fine powder
0.0001 cm. = 1 μ	10 ¹²	6 m. ²	microscopic	very fine powder
0.00001 cm.	10 ¹⁶	60 m. ²	ultramicro-	colloids
0.000001 cm.	10 ¹⁸	600 m. ²	scopic	colloids
0.0000001 cm. = 1 $\mu\mu$	10 ²¹	6,000 m. ²	amicroscopic	colloids
0.00000001 cm.	10 ²⁴	60,000 m. ²	or invisible	molecules

(a) 1 m. (meter) = 100 cm. (centimeter) = 1,000 mm. (millimeter) = 1,000,000 μ (microns) = 1,000,000,000 $\mu\mu$ (millimicrons) = 39.37 inches.

(b) 10³ = 1,000; and 10²⁴ = 1,000,000,000,000,000,000,000,000.

(c) Cm.² = cm. $\times$ cm. = square centimeter; m.² = m. $\times$ m. = square meter.

(d) Blood corpuscles 7.5 to 15 μ , bacilli 1 to 10 μ , hydrogen molecules 0.20 $\mu\mu$, chlorine molecule 0.40 $\mu\mu$.

Colloids.—Finely divided substances usually react faster than coarse ones. For this reason finely powdered substances and substances in the colloidal state are reactive, as well as gases and substances in solutions. Colloids are simply finely divided particles of ultramicroscopical size which form the transition from single molecules to aggregations of molecules of microscopical size.

Increase of Surface by Melting.—A reaction may also be started when the surface of contact between two solid substances is increased, not by subdivision, but by melting one substance. Thus in Fig. 2 it is evident that the points of contact between two substances is restricted when both are solid particles, but is greatly increased when one substance is liquid. An example is furnished by finely divided sulfur and iron, which can be kept mixed

together indefinitely without a reaction occurring. As soon, however, as the sulfur is molten, the reaction begins. In this case not only the number of sulfur molecules and iron molecules colliding with each other has increased, but another factor, heat, has been introduced, the effect of which forms the subject of a later paragraph.

Catalyzers.—A reaction may also be either accelerated or retarded by the presence of a third substance, a catalyzer or catalyst, which is, or appears to be, unchanged throughout the reaction but whose presence is essential for the procedure of the reaction. The action of a



FIG. 2.—Increasing the surface by melting.

catalyzer is either of a mechanical or chemical nature. The mechanical catalyzers are such substances which, when finely divided, have the property to adsorb upon their surface the molecules of other substances. Thus, finely divided palladium will adsorb hydrogen gas and the surface of the metal will be covered with a layer of hydrogen molecules. These densely packed hydrogen molecules are much more reactive than the widely scattered hydrogen molecules in hydrogen gas—in other words the hydrogen molecules have been concentrated and the gas has been condensed to a solid substance. Many important processes in industrial manufacture depend upon the use of catalyzers (fixation of atmospheric nitrogen, manufacturing sulfuric acid, etc.).

Mass Action.—The dependence of a chemical reaction on the concentration of the molecules is expressed in the law of mass action by Guldberg and Waage which holds that the chemical effect of molecules participating in a chemical reaction is proportional to their mass, that is, the amount or number of molecules present in a certain volume. In the case of solutions this mass is expressed as *concentration* which is the amount of substance (gram-molecules or moles) dissolved in a given volume of solvent (1 liter). In the case of gases this mass is expressed as pressure, for the pressure is an indication of the number of molecules present in a

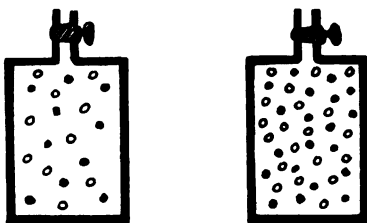


Fig. 3.—Increasing the surface by concentration or pressure.

certain volume of a gas. This is best illustrated by Fig. 3 in which there is in one case 10 molecules each in a given volume, and in the second case 20 molecules each in a given volume. The kinetic theory assumes that the molecules of a gas are in free movement and will therefore collide and bombard the sides of the vessels. The sum of these impacts upon the walls of the container is shown as pressure, hence by doubling the number of molecules in the same volume, the pressure is doubled, for the number of collisions and impacts has been doubled. It has been found that under normal conditions (atmospheric pressure of 760 mm. at 0°C., and at sea-level) one mole of any gas will occupy a

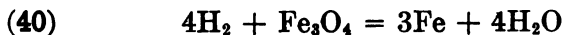
volume of 22.4 liters. (A mole is the molecular weight of a substance in grams, that is, a mole of H_2 is 2 grams, a mole of O_2 is 32 grams, etc.) The kinetic theory of gases has been extended to molecules in solutions which means that the molecules and ions in a solution are also free moving and exert pressure—the osmotic pressure.

Pressure.—The more moles there are in a liter of gas or a liter of solution, the more molecules there are in this unit volume, and the higher the concentration or pressure, hence the greater the possibility for the molecules to collide and react. The tendency to react is generally increased with an increase in the number of molecules or ions present in a certain volume; but as, during the reaction, some of these molecules or ions have been used up or exhausted by being transformed, their concentration becomes less as the reaction proceeds, yet, at the same time the concentration of the reaction products is increased and the tendency to again form the original molecules becomes greater. A chemical reaction therefore is never complete if the reaction products can again form the original substances. If two molecules (AB and CD) react to form two other molecules (AD and CB) as reaction products, then after a certain time there will be a chemical system in which all four types of molecules (AB , CD , AD , and CB) are present. The percentage of the different molecules will depend upon the speed of the reactions $AB + CD \rightarrow AD + CB$ and $AD + CB \rightarrow AB + CD$. It is evident that the speed of the first reaction is greatest at the beginning, for the reaction is started with a high concentration of AB and CD , and the absence (zero concentration) of AD and CB , but this speed will diminish more and more as the reaction products AD and CB

are formed. The speed of the second reaction is at first null, as no AD and CB is present, but this speed increases slowly with an increase in the amount or concentration of AD and CB . As the speed of the first reaction diminishes and the speed of the second reaction increases, there will come a time when the speed of both reactions are equal, and a chemical equilibrium is established.

Equilibrium.—In a chemical equilibrium the visible effects of a reaction are at stand-still and the reaction appears to have stopped, this does not imply, however, that the molecules have ceased to collide with each other. The molecular collisions still take place, but the formation of AB and CD has become equal to the formation of AD and CB , in other words the exchange of the constituents of the molecules is balanced. The same condition of equilibrium is reached when the original substances are AD and CB instead of AB and CD . Under definite conditions (temperature, concentration or pressure) there is for any system of substances only one equilibrium which is established whether the reaction is started with AB and CD or with AD and CB .

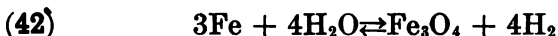
Example of Equilibrium.—A concrete example is given by the following experiment. In one closed vessel hydrogen gas and ferrous-ferric oxide is heated, and in another closed vessel iron granules and steam (water). After heating a certain time and keeping at a certain temperature, *both* vessels will contain the same proportion of hydrogen gas to steam. In the first container the reaction was



while in the second vessel the reaction was

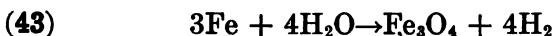


Accordingly one reaction is the reverse of the other, a fact which can be expressed by using the sign of a reversible reaction, namely two arrows:

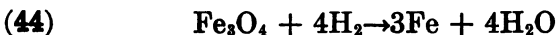


In both cases the same equilibrium was obtained, though the original substances were different. The percentage of steam and hydrogen will depend upon temperature, but at the same temperature this percentage is the same in both cases.

Shifting the Equilibrium.—The experimental conditions can be so arranged that during the reaction one or the other of the gases is removed. In this case the removal of one gas will constantly shift or destroy the equilibrium, and the reaction may proceed to completion. Thus by heating the iron granules in a tube open at one end, and passing a strong current of steam into this tube, hydrogen gas will emerge from the open end until all the iron is oxidized. In this case the hydrogen molecules, as soon as formed, are carried away and thus removed by the excess of steam flowing into the tube, and the reaction will be complete in one direction:



The concentration of hydrogen molecules under these conditions was never high enough to initiate the reverse reaction. On the other hand if the tube is filled with ferrous-ferric oxide and a stream of hydrogen gas is passed into it, steam will be formed until all the iron oxide is reduced to metallic iron:

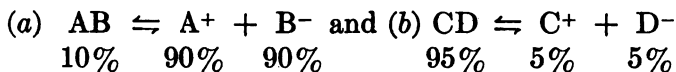


In this case likewise the reaction product, steam, as soon as formed, is carried away by the current of hydro-

gen gas and the reduction of the iron oxide will proceed completely.

Speed of Reaction.—Theoretically, the speed of a chemical reaction is greatest in the beginning but diminishes more and more as the reaction proceeds. As a rule ionic reactions are instantaneous, that is, their speed is too rapid to measure. Molecular reactions are slower and their speed can be measured and controlled as in the preceding example. Some reactions are too slow to measure, *i.e.* the oxidation of iron in air at ordinary temperature. By increase of concentration (or temperature) these reactions will proceed faster, *i.e.* burning of iron wire in oxygen.

Ionic Equilibrium.—The control of an ionic reaction depends upon the same principle, for the reaction will take place whenever the ionic equilibrium is disturbed or shifted by changing the concentration or the amount of ions present in a unit volume. Assuming for example that two compounds, AB and CD, are each separately dissolved in certain amounts of water and measurements show that the first solution contains 90 per cent ions while the second solution contains only 5 per cent ions, then an ionic equilibrium has been established which can be expressed by the equations:



It is evident that in solution *a* there are 18 times as many ions as molecules, hence the substance AB is said to be highly or strongly ionized; while in solution *b* there are nearly ten times as many molecules as ions, hence the substance CD is little or weakly ionized. In both cases the speed of the reaction from left to right and from right to left has become equal. Such an ionic equi-

brium, which is formed whenever a substance is dissolved in water, is disturbed by either adding or removing AB, A^+ , or B^- to or from solution (a), or by adding or removing CD, C^+ , or D^- to or from solution (b). The addition or removal of molecules or ions is accomplished by: (a) adding more molecules by dissolving more of the substance, (b) diluting the solution, (c) removing some ions in the form of molecular or non-ionized soluble compounds (like water, weak acids, weak bases, or weak salts), (d) removing some ions in an insoluble compound (precipitates), (e) removing some ions in a gaseous compound (gas bubbles), (f) the formation of complex ions. In each case the ionic equilibrium is shifted.

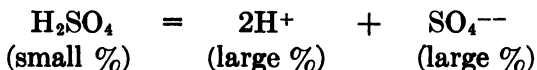
Formation of Water.—Neutralization means the adding of H^+ to an ionic equilibrium containing OH^- whereby water is formed, and as water is practically not ionized, the removal of H^+ and OH^- from the ionic equilibrium will be practically complete, that is a reaction will take place until all H^+ or OH^- present have been used up. Therefore whenever there is the possibility that water can be formed from two solutions a reaction is likely to take place.

Formation of Precipitate.—In precipitation a molecular and insoluble compound is formed from ionic constituents and by this precipitate certain ions are taken from the solution and thereby the ionic equilibrium is shifted. The ionic equilibrium $BaCl_2 = Ba^{++} + 2Cl^-$ can be made to proceed from left to right by either (a) adding more barium chloride, (b) removing Ba^{++} as a precipitate ($BaSO_4$) by the addition of SO_4^{--} , or (c) removing Cl^- as a precipitate ($AgCl$) by adding Ag^+ . In the last two cases the ions have been removed by a precipitate hence more of the molecular barium chloride

will ionize, and if sufficient SO_4^{--} or Ag^+ is added, all of the ions may be precipitated, and thereby the reaction controlled.

Formation of Gas.—An ionic equilibrium is likewise shifted by the formation of a gas from certain ions, and the liberation of the gas will remove certain ions from the solution. Thus, by adding an acid (H^+) to a solution of sodium sulfide $\text{Na}_2\text{S} = 2\text{Na}^+ + \text{S}^{--}$, the formation of gaseous, non-ionized hydrogen sulfide will remove the S^{--} from the equilibrium, hence more Na_2S will ionize and, if sufficient acid is added, all of the sulfide ions may be removed as H_2S . Such reactions can be accelerated by mechanical means (*e.g.* agitation or passing a current of air through the solution) or thermal means (*e.g.* heating) or both together, for by these means the escape or liberation of the gas from the solution is facilitated.

Formation of Weak Acids.—The formation of weak acids (acids which are little ionized) will remove hydrogen ions. A solution of sulfuric acid contains much H^+ , that is,

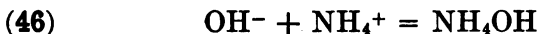


and when this is added to a soluble acetate, citrate, oxalate, or other salts of a weak acid, the acidity or hydrogen ion concentration will be reduced, as the respective slightly ionized acetic acid, citric acid, or oxalic acid is formed:



To illustrate this by experiment, fill a test tube with very dilute sulfuric acid and color it with an indicator (litmus, methyl orange, methyl violet, congo red, etc.), if the neutral salt (*e.g.* sodium acetate, sodium citrate) is added, the color will change and indicate a neutral reaction.

Formation of Weak Bases.—The formation of weak bases (bases which are little ionized) will remove hydroxyl ions. Thus when a solution of sodium hydroxide (strong base) containing a large percentage of OH^- , is added to a solid ammonium salt, the reaction product will be ammonium hydroxide (weak base) which is but little ionized:



Try the following experiment: Color a diluted sodium hydroxide solution with a few drops of indicator and add some ammonium sulfate or ammonium chloride—note the change in color.

Formation of Weak Salt and Complex Ion.—A weak salt is a compound which, while soluble, is little ionized, $\text{MN} \rightleftharpoons \text{M}^+ + \text{N}^-$, with a large percentage of MN , and a very small percentage of M^+ and N^- . If such a compound is formed during a reaction its formation will remove certain anions and cations and thereby destroy the ionic equilibrium. Likewise the formation of complex ions destroys the ionic equilibrium by the removal of ions. A complex ion is a charged group of atoms or an ion combined with a neutral molecule, such as the ammonia complexes $\text{Cu}(\text{NH}_3)_4^{++}$, $\text{Ni}(\text{NH}_3)_4^{++}$, $\text{Ag}(\text{NH}_3)_2^+$, etc.; the cyanide complexes $\text{Cu}(\text{CN})_2^{++}$, $\text{Ni}(\text{CN})_4^{++}$, etc.; certain halogen compounds, oxalates, ferro- and ferricyanides, etc.

Prediction of Reaction.—To summarize the facts of ionic equilibrium and ionic concentration: A reaction is likely to occur whenever there is a possibility that the ions of two different molecules in solution (ionic equilibrium) may form (a) water, (b) precipitate, (c) gas, (d) weak acids, (e) weak base, (f) weak salt, or (g) complex ions, for by the formation of these substances the ionic concentration is changed (decreased). By applying

this rule it can be predicted whether or not a reaction will occur if two substances in solution are brought together.¹

THE THERMAL CONTROL

Increase or Decrease of Temperature.—The thermal means which influence the frequency of molecular collisions are those by which not the number but the velocity of the molecules is regulated. The faster the molecules move the more numerous are the collisions; the slower their movement, the less becomes the frequency of collisions. Heat or a rise in temperature increases the molecular movement, hence increases the number of molecular collisions and therefore accelerates a reaction. A rise of 10°C. will generally double the speed of a reaction.

States of Aggregation.—It is assumed that the three states of aggregations, solids, liquids, and gases, are due to the rate of vibrations of the molecules. In solid and liquid substances the vibrations are comparatively slow, while in dissolved and gaseous substances the vibrations are fast and the molecules can move freely. The change from the solid to the liquid state, and from the liquid to the gaseous state is thus always a change from slower to faster vibrating molecules. Any change in the velocity or vibrating speed of the molecules manifests itself either in an absorption or liberation of heat. We speak therefore of heat of fusion or melting as well as heat of vaporization and mean thereby the amount of heat necessary to transform a solid at its melting point into a liquid, or a liquid at its boiling point into a gas.

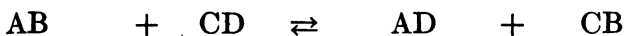
Exothermic and Endothermic.—During a chemical reaction heat may be produced or consumed. If the

¹ For a full discussion of the control of chemical reactions and equilibrium see Hildebrand's Principles of Chemistry, Chaps. xi-xiv.

reaction liberates heat (exothermic reaction) then a compound (exothermic compound) has been formed as reaction product which contains less heat than the previous molecules, for the molecules of one or the other reaction product will vibrate at a lower speed than the original reacting substances. Such molecules of exothermic compounds are, as a rule, stable and not readily decomposed. If, on the other hand, during a reaction a certain amount of heat is used up (endothermic reaction) then a compound (endothermic compound) has been formed whose molecules vibrate more rapidly. Endothermic compounds are, as a rule, unstable and may decompose so rapidly as to cause explosions. The relation between these two types of reactions and compounds is shown in the sketch:

EXOTHERMIC REACTION

(proceeds rapidly from left to right and liberates heat)



ENDOTHERMIC COMPOUNDS	EXOTHERMIC COMPOUNDS
(unstable)	(stable)

ENDOTHERMIC REACTION

(proceeds slowly from right to left and absorbs heat).

An exothermic reaction is the change from endothermic to exothermic compounds—from faster to slower vibrating molecules. This change requires no heat, only an external start and the reaction will proceed rapidly and completely with the liberation of heat, it may be even explosive. An endothermic reaction is the change from an exothermic to endothermic compound,—from slower to faster vibrating molecules. This change

requires a constant influx of heat and the reaction will proceed slowly and be limited by the tendency of the reaction products to again decompose (dissociation).

The general tendency of chemical reactions is to produce exothermic compounds, that is, reaction products which develop the largest amount of heat (Thomson's rule, Berthelot's principle). In other words, rapidly vibrating molecules have the tendency to rearrange themselves and form slower vibrating molecules, thereby liberating a definite amount of heat. However if external heat is applied to two exothermic compounds, their molecular vibrations may be accelerated sufficiently to form an endothermic compound.

Control of Velocity.—The rise or fall of temperature therefore is a means to increase or decrease the velocity of molecular vibrations which in turn controls the speed of molecular reactions. The application of heat generally has no effect upon ionic reactions.

It is also evident that the increasing velocity of molecular vibrations can aid combination as well as decomposition, or dissociation. Dissociation or the breaking apart of molecules may be caused by the two external means—heat and electricity. The thermic dissociation (commonly called dissociation) is produced by higher temperatures and continues only as long as the external cause (heat) is active; the electric dissociation (properly called ionization) is produced by dissolving electrolytes.

Dissociation.—Thermic dissociation proceeds slowly with the rise of temperature and diminishes accordingly with a fall of temperature. *I.e.* hydrogen and oxygen begin to combine at 200°C. and form steam; at 1,200°C. dissociation begins, for some molecules of H_2O will decompose into hydrogen and oxygen; at 2,500°C.

there is about half of the steam dissociated into H_2 and O_2 , and with a further rise of temperature all the molecules of steam are finally dissociated. By lowering the temperature combination takes place again and at $1,200^\circ C$. only steam will be present.

Dissociation does not depend solely upon temperature, but also upon pressure. Increase in pressure diminishes, while a decrease in pressure increases dissociation. For each definite pressure at a definite temperature the amount of dissociation, that is, the percentage of dissociated molecules of the same substance will be constant. The dissociation may be diminished by adding more of one of the gaseous components, for then the equilibrium is shifted by the introduction of a larger amount of one gas. Dissociation is not restricted to gaseous compounds and another example that heat can combine as well as decompose is the classical experiment of Lavoisier of making oxygen from mercuric oxide. At ordinary temperature mercury is not attacked by the oxygen of the air, but heating slowly transforms it into mercuric oxide, and if heated to a higher temperature, it decomposes again into mercury vapor and oxygen.

The explanation of dissociation is found in the assumption that not only the molecules but also the atoms are in movement or rather vibrating. Therefore a rise of temperature will not only increase the speed of the molecules, but will also increase the speed of the vibrations of the atoms, and finally the atomic vibrations will become so rapid that the atoms will leave their attraction spheres and travel as independent units—thus splitting the molecules.

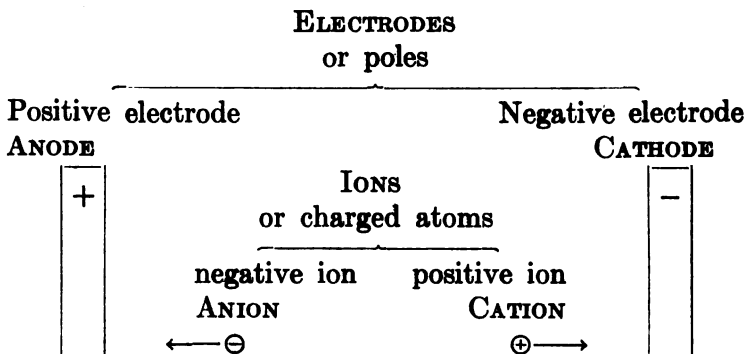
Action of Light.—The action of light is probably of a similar nature. Light rays either combine or decompose. Thus a mixture of Cl_2 and H_2 when kept in the dark

remains unchanged, but if brought into bright sunlight, the gases may combine so suddenly that the mixture explodes. The action of light upon the photographic plate and the bleaching of aniline dyes are examples of decomposition by light.

THE ELECTRICAL CONTROL: Electro-motive Force

The electrical means which influence a chemical reaction depend upon the control of the electro-motive force or potential energy. The relationship between chemical and electrical energy is close and there are various ways to transform one into the other and vice versa.

Electrolysis.—The transformation of electrical into chemical energy is illustrated by the phenomena of electrolysis and displacement. When an electric current is passed through a molten or dissolved electrolyte, that is, any substance which conducts the current, separation or electrolysis takes place. The terms employed in electrolysis are illustrated in the sketch:



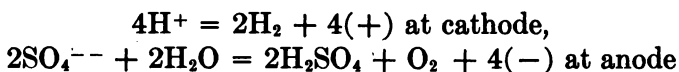
Electrolysis can take place only when the electrolyte is either molten or dissolved, that is, already more or less dissociated or split into ions; hence it is not a decomposi-

tion of the electrolyte but merely a separation of the ions already present. The cause of this separation or migration of the ions to the poles or electrodes is found in the charge of the atoms. The anions are negatively charged atoms and will migrate or move to the anode or positive pole, while the cations or negatively charged atoms move toward the cathode or negatively charged electrode and there deliver their charges. The charges of the ions are taken up by the electrodes or poles and the ions which lose their charge are then deposited as atoms or molecules of the free elements.

In the electrolysis of any acid the hydrogen is found at the cathode, and the acid radical at the anode. In the electrolysis of any base the metal is liberated at the cathode, while the hydroxyl group moves to the anode. In the electrolysis of any salt its metallic constituent is found at the cathode, while the non-metal or acid radical is deposited at the anode. Thus hydrogen and metals are considered positive elements, while non-metals and acid radicals are negative elements or radicals. The atoms or group of atoms deposited at the electrodes and deprived of their charges can not exist in free state, hence will combine and form molecules.

Secondary Reaction Products.—In many cases these newly formed molecules react either with the material of the electrode or with the solvent producing new compounds as secondary reaction products. In such cases, not the elements of the electrolyte, but secondary reaction products are found. If an electric current is passed through a solution of sodium chloride (electrolyte), the sodium (cation) migrates to the negative electrode (cathode), and the chlorine (anion) moves to the positive electrode (anode) and forms respectively sodium metal and chlorine gas, but these free elements

both react with water and thus give sodium hydroxide, at the cathode and at the anode hydrochloric acid and hypochloric acid. These important secondary reaction products account for many phenomena and their formation is utilized in many industrial processes for the manufacture of chemicals. Formerly it was believed that the electric current electrolyzed or decomposed water into hydrogen and oxygen gas. Now we know that absolutely pure water is a very poor electrolyte and will not conduct the electric current, hence it cannot be decomposed. However if an electrolyte is added, *i.e.*, if the water is acidulated with sulfuric acid, then these two gases will be produced, not as primary, but as the secondary reaction products. What really happens is the decomposition of the sulfuric acid which is dissociated or ionized into the cations H^+ and anions SO_4^{--} . The electric current simply separates these ions locally and the H^+ of the sulfuric acid delivers its charge at the cathode and forms H_2 molecules; while the anions SO_4^{--} migrate to the anode, deliver their charges, and react with water to form sulfuric acid and oxygen:



Combining these two reactions and cancelling the sulfuric acid there remains:



which is the visible part of this electrolysis, for when the gases are collected the volume of hydrogen will be exactly twice the volume of oxygen. The sulfuric acid formed at the anode dissociates again:



and its respective cations and anions migrate once more to the cathode and anode and repeat the process. In the electrolysis of acidulated water there is thus a continuous dissociation and combination of the acid in which the constituents of water take part, and by which hydrogen and oxygen are formed as secondary reaction products.

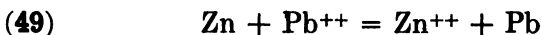
Electrochemical Equivalent.—The amount of substance deposited or liberated at the electrodes depends upon the amount of electricity which passes through the solution. The amount of electricity is measured in coulombs or ampere-seconds. The same quantity of electricity in the same length of time will separate the ions at both electrodes in proportion to their equivalent weight (Faraday's rule). The equivalent weight is the atomic weight divided by the valency. To deposit a gram equivalent (atomic weight/valence = x grammes) of any ion requires 96,540 coulombs. Hence of copper (Cu^{++}) $63.6/2 = 31.8$ grams, of silver (Ag^+) 107.0 grams, of ferrous ion (Fe^{++}) $56/2 = 28$ grams, of ferric ion (Fe^{+++}) $56/3 = 18.7$ grams will be deposited by 96,540 coulombs. The total electrical charge on a gram equivalent of any ion is therefore 96,540 coulombs as this amount of electricity is required to neutralize the total charge of the gram equivalent; and the total charge on a mole or gram atom of an ion is 96,540 times its valency.

Electro-motive Force.—The force with which the ions hold this charge is called electro-affinity or electro-motive force. This force varies for different ions. To the strong ions belong the cations K^+ , Na^+ , Li^+ , and the anions NO_3^- , F^- , Cl^- , SO_4^{--} ; while to the weak ions belong the cations Hg^{++} , Au^{+++} , Pt^{++++} , and the anions O^{--} , S^{--} , CN^- . (It is well to note the distinction

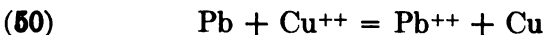
between the ionic charge and the force with which the ionic charge is held.)

A substance of strong electro-motive force is one which produces strong ions, that is, the atoms hold the electrical charge firmly. A substance of weak electro-motive force is one whose atoms hold the electrical charge less firmly, and thus gives weak ions.

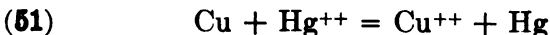
Displacement.—If a substance capable of yielding strong ions be added to a solution of weak ions, then the weak ions will give up their charge and become electrically neutral, while the solution will contain the strong ions. When a piece of metallic zinc (strong electro-motive force) is placed in a solution containing lead ions (weak electro-motive force), zinc ions are formed, and metallic lead is deposited as a black spongy mass:



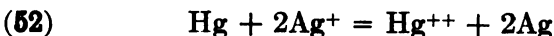
Metallic lead in turn will precipitate copper (weaker electro-motive force) from a solution of cupric ions:



Metallic copper will discharge mercuric ions and deposit mercury:

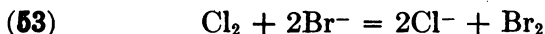


The weak electro-motive force of mercury is stronger than the electro-motive force of silver, therefore it will take the ionic charge from the silver ions and crystalline silver will be deposited:

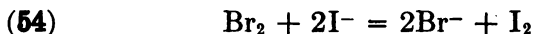


In the same manner electro-negative elements of stronger electro-motive force will become ionized and form anions if they come in contact with anions of

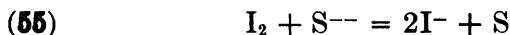
weaker electro-motive force, hence chlorine gas will react with bromine ions:



Bromine will react with iodide ions:

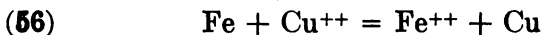


Iodine is stronger than sulfide ion:



Displacement Series.—The sequence in which the elements act in this manner is according to the preceding equations for the positive metals $\text{Zn} > \text{Pb} > \text{Cu} > \text{Hg} > \text{Ag}$, and for the negative non-metals $\text{Cl} > \text{Br} > \text{I} > \text{S}$. Zinc is thus more positive than silver, and silver more negative than zinc. Chlorine is more negative than sulfur, or sulfur is more positive than chlorine. Positive and negative are thus relative terms and it is possible to place all elements in such a relative series which is termed the displacement series. In the displacement series, given in the appendix, the most negative elements are at the beginning, and these will displace as anions all that follow; while the elements at the end are the most positive and will displace as cations all above them.

From the above it becomes evident that, if a piece of iron is dipped into a copper salt solution, metallic copper will be deposited and the iron will go into solution:



The cupric ion has given its charges to the iron and has become electrically neutral copper, while the previously electrically neutral iron has taken this charge and become ferrous ion. This transmission of the electric charge takes place simultaneously and may occur at any point of contact between the iron and the copper ions.

Voltaic Cells.—The transformation of chemical energy into electrical energy is demonstrated by voltaic cells or batteries. Thus the experimental conditions of the above reaction (56) can be so arranged that the direct contact of iron and copper ions is prevented, but the exchange of the charges or electrons is made possible by a conducting connection between the iron and the copper ions which causes a stream of electrons to pass, thus producing an electric current in the conducting connection (metal

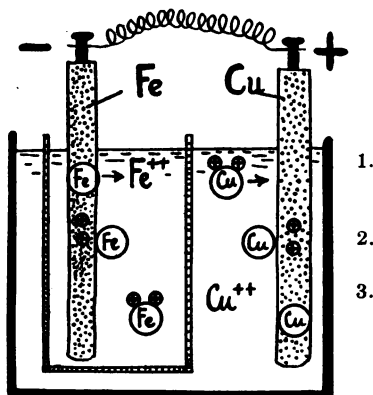


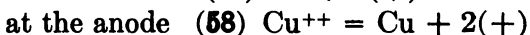
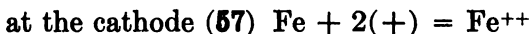
FIG. 4.—A voltaic cell or electrical battery.

wire). These experimental conditions are illustrated in a galvanic battery or voltaic cell. It is essential in such experimental conditions that the reacting substances are locally separated, yet connected by a conducting media, for only then are the electrons forced to travel through the conductor and produce an electric current when the circuit is closed. The conditions are schematically represented in Fig. 4.

The farther apart the two metals selected as electrodes stand in the displacement series, the greater will be the produced electro-motive force or potential, measured in

volts. Hence Fe and Zn will produce a smaller voltage than Al and Pb or Mg and Cu; likewise Zn and Cu or Zn and Ag will produce a greater voltage than Zn and Fe.

Example of Cell.—In the figure a rod of iron and a rod of copper are used as electrodes. The iron stands in a solution of ferrous sulfate, the copper in a solution of cupric sulfate, and the solutions are separated by a porous wall or semi-permeable membrane. If the concentration of the ferrous sulfate solution is low, and the concentration of the copper sulfate solution is high—the metallic iron tends to go into solution, that is, acquire two positive charges and thus form ferrous ions, while, at the same moment, a cupric ion will deliver two positive charges to the copper rod and be deposited as metallic copper. The iron rod will lose weight; the copper rod will gain weight. The iron electrode becomes “less positive” that is “more negative,” and the copper electrode becomes more positive. The reactions which take place are:



and by adding these two equations, and cancelling the two positive charges which appear on both sides, equation (56) results.

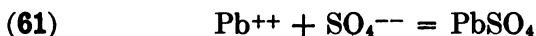
Both reactions (57 and 58) occur simultaneously and proceed until an equilibrium is established, and the current ceases. If the ferrous ion concentration is very low in the beginning and the cupric ion concentration very high, the battery will live longer. If, however, at the beginning the ferrous ion concentration is high, and the cupric ion concentration is low, little or no current will be produced.

Secondary Cells.—By the proper selection of the materials used as electrodes and solutions, many of the batteries can be arranged so that the reaction is reversible. In such a case an electric current passed through the cell in the reverse direction will cause the reverse reaction and the original state will be resumed. Such would be the case in Fig. 4 if the copper were connected with the negative pole of a dynamo, and the iron with the positive pole so that electrolysis would take place. Such a battery is called a secondary cell or accumulator.

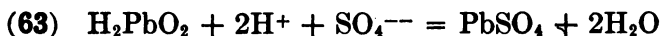
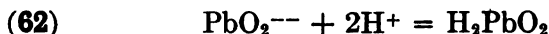
Accumulator.—At present the lead accumulator is the most practical secondary cell for common use. In discharging this accumulator, the lead is the cathode, the lead oxide the anode, and the following reaction takes place:



Thus at the cathode the lead will dissolve and send positive lead ions into solution, and the cathode becomes less positive—hence negative. From the anode negatively charged PbO_2^{--} ions go into solution, and the anode thus loses negative charges or electrons, it becomes less negative,—hence more positive. As there is an excess of sulfuric acid in the accumulators the lead ions form insoluble lead sulfate:



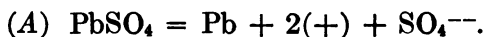
The plumbate ions formed at the anode react with the hydrogen ions of the sulfuric acid and give plumbic acid, which in turn reacts with the sulfuric acid and yields ultimately lead sulfate.



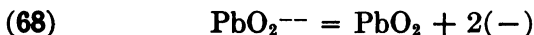
The endproduct in both cases is thus lead sulfate and theoretically the accumulator is entirely exhausted or discharged when all the lead and lead oxide has been transformed into lead sulfate; but practically this condition never happens as the reaction is reversible. When an accumulator is exhausted a chemical equilibrium is established in which the reactions 59 to 63 have ceased and a large amount of lead sulfate is present. By passing an electric current from an outside source through the accumulator the lead sulfate is decomposed again into Pb and PbO₂, as the reactions have been reversed. In charging the accumulator the reactions are at the anode



Adding these two reactions together:



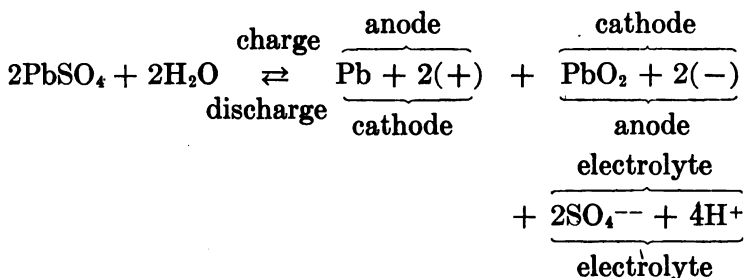
The reactions at the cathode are:



Adding these three reactions together:



and comparing equation (A) with (B) we find the two negative charges liberated in (B) counterbalanced by the two positive charges of (A). By the addition of (A) to (B) it is possible to represent the reactions occurring at the electrodes during charge and discharge of the accumulator:



Chemical Affinity.—The preceding paragraphs show the influence of mechanical, thermal, and electrical means and the corresponding phenomena have been discussed as mass action, kinetic or free energy, and electro-motive force of the atoms. However some reactions are affected by another factor which can not be grouped under these three headings. This fourth factor depends upon the nature of the substance and is expressed by a certain selective tendency or chemical affinity of one type of atoms for another type of atoms. The chemical affinity manifests itself in certain elements which are grouped together in the periodic chart (see appendix). Thus the elements located around boron have an affinity for nitrogen and yield nitrides (BN, etc.), while those in the neighborhood of lithium have an affinity for hydrogen and give hydrides (LiH, etc.). The reason of chemical affinity is not due to electro-motive force and is yet unknown.¹

Summary.—By physical means (mechanical, thermal, electrical) the speed of a reaction can be (a) accelerated, (b) retarded, (c) stopped, or (d) reversed.

Mechanical means when applied to ionic and molecular reactions control the number of molecules per unit volume: (a) subdivision of solid substances (colloids), (b) concentration of solutions, (c) pressure of gases, (d)

¹ For a discussion of affinity see American Journal of Science, vol. 46, page 490, 1918.

catalysers. In molecular reactions an increase in the number of molecules will increase the frequency of molecular collisions and thereby increase the possibility of reaction. In ionic reactions the control of the concentration is brought about by the removal of anions or cations; thus the possible formation of (a) water removes H^+ and OH^- , (b) precipitate removes either cation or anion, (c) gas removes either cation or anion, (d) weak acid removes H^+ , (e) weak base removes OH^- , (f) weak salt removes cation or anion, (g) complex ions remove cation or anion.

Thermal means are generally applied to molecular reactions and consist in control of temperature or the velocity of molecular vibrations. Raising the temperature increases the velocity of the molecules, thus increasing the frequency of molecular collisions and hence accelerating the speed of a reaction.

Electrical means when applied to ionic reactions control the local separation of ions. The density of the electric current will determine the speed of the reaction.

QUESTIONS AND PROBLEMS

1. What will be the effect of (a) little, (b) much water on the hydrolysis of $BiCl_3$ (equation 160)?

2. Write equations for the reaction of bromine with (a) aluminum, (b) iron, (c) magnesium, (d) sodium, and arrange them according to their relative speeds as deduced from the displacement series.

3. By heating the hydroxides and carbonates of (a) calcium, (b) copper, (c) iron, (d) nickel, (e) silver, the respective metal oxides are formed. Write equations and state which compound requires the lowest, and which compound the highest temperature for its decomposition.

4. By adding water to (a) Ca_3N_2 , (b) Ca_3P_2 , (c) Ca_3As_2 , calcium-hydroxide is formed. What are the other reaction products and which of these three reactions will proceed most rapidly and why?

5. By heating aluminum with (a) antimony, (b) arsenic, (c) bismuth, (d) phosphorus, the respective binary compounds are formed. Which compound will require the least amount of heat?

6. If the metals Al, Ga, Fe, In, Mg, Zn, are heated in a current of

chlorine gas, the respective chlorides are formed. Write the equations and state which metal requires the lowest, and which metal requires the highest temperature to start the reaction.

7. By heating TiCl_4 with metallic Zn or Sn, the TiCl_3 is reduced to TiCl_2 and the bichlorides of Zn or Sn are formed. Write equations and state which reaction occurs more readily.

8. Arrange according to velocity the reactions of water with metallic (a) calcium, (b) copper, (c) aluminum, (d) lithium, (e) iron, (f) magnesium, (g) potassium, (h) sodium.

9. GeO_2 can be reduced to metallic Ge with either H_2 or C. Which reaction proceeds more readily? Which compound does hydrogen gas reduce more readily GeO_2 or GeS_2 ? Write equations for each.

10. Predict what will happen if metallic magnesium is heated with (a) SiO_2 , (b) GeO_2 , (c) PbO_2 . Which reaction proceeds more readily?

11. Carbon dioxide can be reduced to carbon by (a) calcium, (b) magnesium, (c) potassium, (d) sodium. Write the equations and arrange them in the order of their speed of reaction.

12. Point out which metals are soluble in sulfuric acid under the evolution of hydrogen gas: (a) aluminum, (b) copper, (c) iron, (d) magnesium, (e) silver, (f) tin, (g) zinc?

13. Which element reduces HAuCl_4 most readily: (a) copper, (b) iron, (c) phosphorus, (d) tin?

14. Arrange the following oxides in the order in which carbon will reduce them most readily to metals: (a) aluminum oxide, (b) iron oxide, (c) lead oxide, (d) magnesium oxide, (e) tin oxide, (f) zinc oxide. Write the respective equations.

15. Give a reason why iodine replaces chlorine in the equation: $2\text{KClO}_3 + \text{I}_2 = 2\text{KIO}_3 + \text{Cl}_2$. (This reaction occurs in the presence of HNO_3 as catalyser).

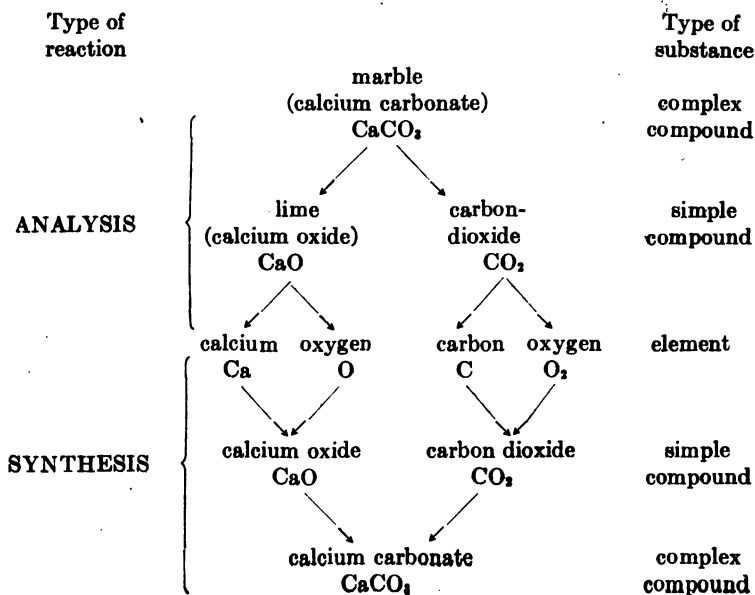
16. By heating metallic Mg and RbOH the following reaction occurs: $2\text{RbOH} + 2\text{Mg} = 2\text{Rb} + 2\text{MgO} + \text{H}_2$. Why is hydrogen gas formed? Why is it not possible for the reaction $\text{Mg}(\text{OH})_2 + 2\text{Rb} = 2\text{RbOH} + \text{Mg}$ to occur?

17. If ammonium bichromate is heated green Cr_2O_3 is formed. What are the possible reaction products? How could you test by experiment whether the oxygen or nitrogen is oxidized? (Write two or more equations of possible reactions.)

CHAPTER VI

TYPES OF REACTIONS AND THEIR EQUATIONS

Reactions and their equations are divided into types. Thus, if a complex molecule is broken apart into simpler or elementary constituents, the process is called *analysis*; the reverse process of constructing or building up complex molecules from elementary constituents is called *synthesis*; while the exchange of parts of one molecule with parts of another molecule is termed *metathesis*. The first two terms are explained by the following scheme:



Analysis in the above example involves the reactions:



while synthesis is expressed by the equations:



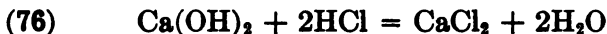
An examination of these two sets of equations reveals the fact that in (69) and (72) there are no changes in the valence number of the elements involved, while in (70), (71), (73), and (74) there is a change in the valence number of the elements, therefore analysis and synthesis may or may not involve oxydation and reduction. It is also evident that (72) is the reverse of (69), (73) the reverse of (70), (74) the reverse of (71). An analytical reaction of type (69) is termed decomposition, while the reverse synthetical reaction (72) is addition—in these two types there is no change of valency. The analytical reaction of type (70) or (71) is known as reduction, while the reverse synthetical reaction (73) or (74) is usually termed oxydation. But the terms oxydation and reduction are ambiguous for they also mean an increase or decrease in the valence number of an element, therefore it is more exact to use combination for oxydation, and division for reduction when speaking of reactions.

An example of metathesis:



shows that there is an exchange of parts in a molecule without change in the valence number. One of the most common types of metathetical reactions is neutralization which has previously been defined as the reaction

between an acid and a base to give water and a salt. An example is:



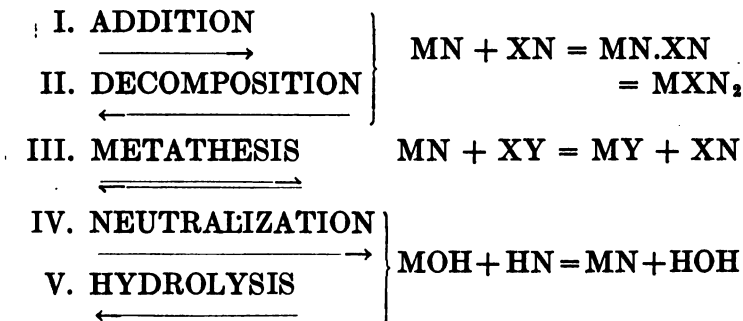
while the reverse reaction is hydrolysis:



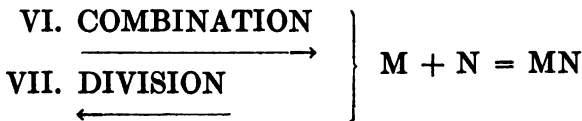
The interrelation of these different types of reactions is shown in the following diagram in which the arrow indicates the direction of the reaction, M and X a metal or positive radical, N and Y a non-metal or negative radical.

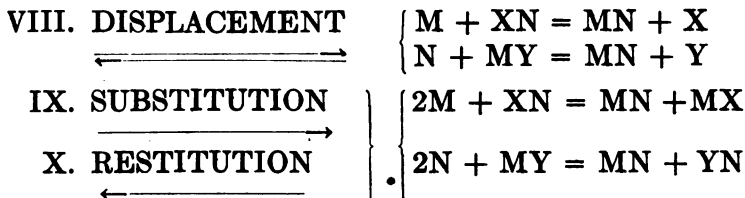
TYPES OF REACTIONS

A. Reactions involving no oxidation and reduction (*i.e.* no increase or decrease in the valence numbers of the elements):



B. Reactions involving oxidation and reduction (*i.e.* increase or decrease in the valence numbers of the elements):

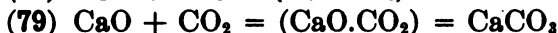
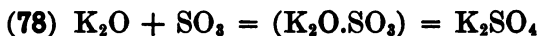




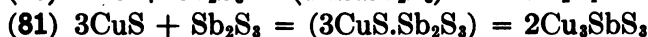
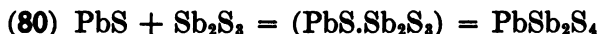
Examples of these ten types of reactions are given in the text and later the complex reactions are discussed. Complex reactions are those which involve two or more types of reactions.

I. ADDITION

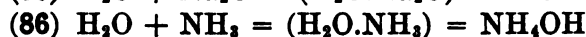
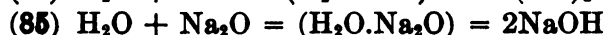
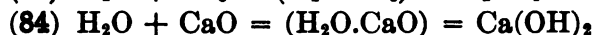
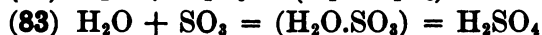
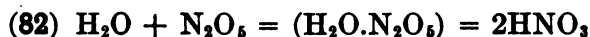
Ordinarily two binary compounds combine and form a more complex compound. The general type is $MX + NX = MX.NX = MNX_2$. The oxysalts of metals are addition products:



Many sulfides form compounds of this type:



Some acids and bases may be considered addition products of water and a metallic or non-metallic oxide:



Other compounds belonging to addition products are:



- (88) $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$
 (89) $\text{Ni}^{++} + 6\text{NH}_3 = \text{Ni}(\text{NH}_3)_6^{++}$
 (90) $\text{Cu}^{++} + 4\text{NH}_4\text{OH} = \text{Cu}(\text{NH}_3)_4^{++} + 4\text{H}_2\text{O}$
 (91) $\text{AgCl} + 2\text{NH}_4\text{OH} = 2\text{Ag}(\text{NH}_3)_2\text{Cl} + 2\text{H}_2\text{O}$
 (92) $\text{Zn}(\text{OH})_2 + 2\text{NH}_4\text{Cl} + 4\text{NH}_3 = \text{Zn}(\text{NH}_3)_6\text{Cl}_2 + 2\text{H}_2\text{O}$
 (93) $\text{NaOH} + \text{CO} = \text{NaHCO}_2 \text{ or } \text{HCOONa}$
 (94) $\text{As}_2\text{S}_3 + 3(\text{NH}_4)_2\text{S} = 2(\text{NH}_4)_3\text{AsS}_3$
 (95) $\text{SnS} + (\text{NH}_4)_2\text{S}_2 = (\text{NH}_4)_2\text{SnS}_3$
 (96) $\text{SnS}_2 + (\text{NH}_4)_2\text{S} = (\text{NH}_4)_2\text{SnS}_3$
 (97) $\text{Fe}(\text{CN})_2 + 4\text{KCN} = \text{K}_4\text{Fe}(\text{CN})_6$
 (98) $\text{Zn}(\text{CN})_2 + 2\text{KCN} = \text{K}_2\text{Zn}(\text{CN})_4$
 (99) $\text{Ni}(\text{CN})_2 + 2\text{KCN} = \text{K}_2\text{Ni}(\text{CN})_4$
 (100) $\text{Co}(\text{NO}_2)_3 + 3\text{KNO}_2 = \text{K}_3\text{Co}(\text{NO}_2)_6$

II. DECOMPOSITION

Decomposition is a chemical reaction in which a complex compound is broken apart into simpler compounds without any change in the valence numbers of the elements involved—it is the reverse reaction of addition:

- (101) $\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$
 (102) $\text{Cu}(\text{OH})_2 = \text{CuO} + \text{H}_2\text{O}$
 (103) $\text{H}_4\text{SnO}_4 = \text{H}_2\text{SnO}_3 + \text{H}_2\text{O}$
 (104) $\text{Cu}(\text{NO}_3)_2 = \text{CuO} + \text{N}_2\text{O}_5$
 (105) $\text{Te}(\text{OH})_6 = \text{TeO}_3 + 3\text{H}_2\text{O}$
 (106) $2\text{B}(\text{NH}_2)_3 = \text{B}_2(\text{NH})_3 + \text{NH}_3 = 2\text{BN} + 4\text{NH}_3$

To this type belongs dehydration, which is the reaction taking place when crystals containing water of crystallization are heated and lose part or all of their water. Dehydration usually proceeds in steps, depending upon temperature, thus

beginning at 19°C.:



beginning at 38°C.:



beginning at 112°C.:



beginning at 203°C.:



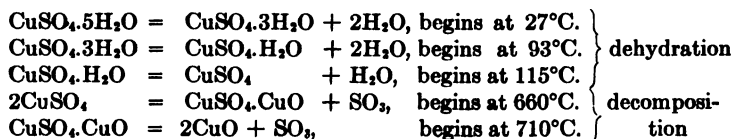
The complete dehydration is expressed by:



In this case the dehydrated magnesium sulfate, when heated to about 400°C., will begin to decompose according to



Many other sulfates behave similarly. The dehydration and decomposition of copper sulfate is expressed in the equations:



The complete dehydration is thus:



and the complete decomposition:

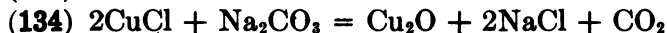
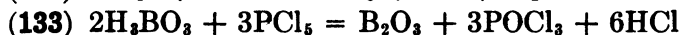
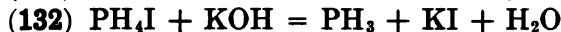
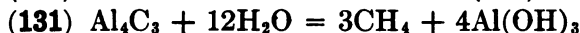
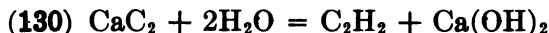
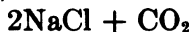
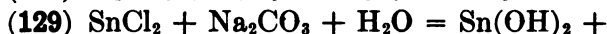
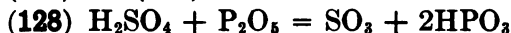
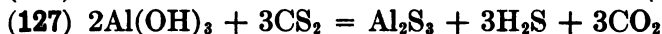
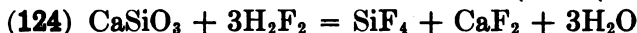
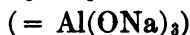


III. METATHESIS

Metathesis is a common reaction. The general type $\text{MN} + \text{XY} = \text{MY} + \text{XN}$ indicates a double decomposi-

tion in which an exchange of the elements or radicals has taken place.

Some examples are:



In the preceding list only molecular equations are given—some of which can be put into ionic form. Typical ionic equations of metathetic reactions are:

- (138) $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$
 (139) $\text{Ba}^{++} + \text{SO}_4^{--} = \text{BaSO}_4$
 (140) $\text{Ba}^{++} + \text{CrO}_4^{--} = \text{BaCrO}_4$
 (141) $\text{Cu}^{++} + 2\text{OH}^- = \text{Cu}(\text{OH})_2$
 (142) $\text{Co}^{++} + 2\text{OH}^- = \text{Co}(\text{OH})_2$
 (143) $\text{Zn}^{++} + 2\text{OH}^- = \text{Zn}(\text{OH})_2$
 (144) $\text{Zn}(\text{OH})_2 + 2\text{OH}^- = \text{ZnO}_2^{--} + 2\text{H}_2\text{O}$
 (145) $\text{Fe}^{++} + 2\text{CN}^- = \text{Fe}(\text{CN})_2$
 (146) $\text{Ni}^{++} + 2\text{CN}^- = \text{Ni}(\text{CN})_2$
 (147) $\text{Zn}^{++} + 2\text{CN}^- = \text{Zn}(\text{CN})_2$
 (148) $2\text{Cu}^{++} + \text{Fe}(\text{CN})_6^{--} = \text{Cu}_2\text{Fe}(\text{CN})_6$
 (149) $\text{Cu}(\text{OH})_2 + 4\text{NH}_4\text{OH} = \text{Cu}(\text{NH}_3)_4^{++} + 2\text{OH}^- + 4\text{H}_2\text{O}$
 (150) $2\text{Na}_3\text{SbS} + 6\text{H}^+ = \text{Sb}_2\text{S}_5 + 6\text{Na}^+ + 3\text{H}_2\text{S}$
 (151) $\text{BaO}_2 + 2\text{H}^+ = \text{Ba}^{++} + \text{H}_2\text{O}_2$
 (152) $\text{PtCl}_6^{--} + 2\text{K}^+ = \text{K}_2\text{PtCl}_6$
 (153) $\text{Cu}^{++} + \text{H}_2\text{S} = \text{CuS} + 2\text{H}^+$

IV. NEUTRALIZATION

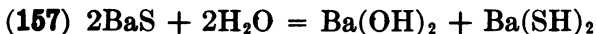
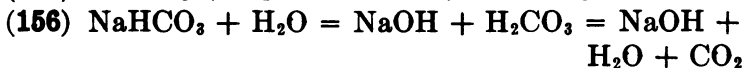
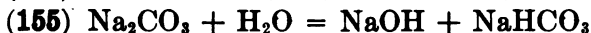
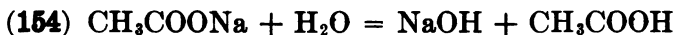
As previously stated, the general equation for neutralization is $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$. This equation is irrespective of the acid and base employed. The salt formed differs in accordance with the acids and bases used, but the formation of water is the principal earmark of neutralization (compare equations 4 to 15). By attaching a negative nonmetal or acid radical, N, to the positive hydrogen ion and to the negative hydroxyl ion a positive metal or basic radical, M, the general type of neutralization is $\text{M}(\text{OH}) + \text{HN} = \text{MN} + \text{HOH}$ and hence it is a metathetical reaction. By substituting any

metal or positive radical for M, and any nonmetal or negative radical for N, a great number of particular reactions are possible, some of which are given in equations 4 to 15.

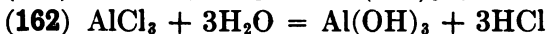
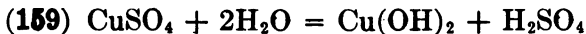
V. HYDROLYSIS

Hydrolysis is a metathetical change brought about by the action of water and is the reverse reaction of neutralization,—the general type is $MN + HOH = M(OH) + HN$. Hydrolysis takes place when the salt of a weak acid, of a weak base, or a compound, whose constituents are not far apart in the displacement series, is dissolved or brought into contact with water.

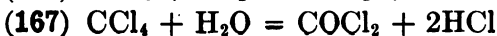
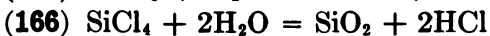
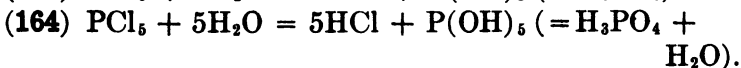
Hydrolysis of salts of a weak acid:

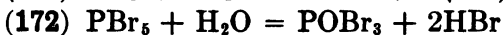
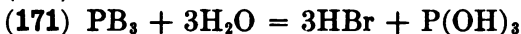
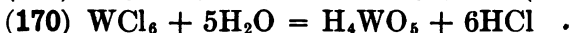
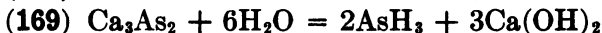


Hydrolysis of salts of a weak base:

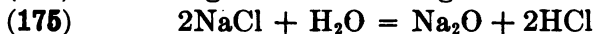
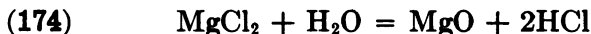


Hydrolysis of compounds whose constituent elements are not far apart in the displacement series:





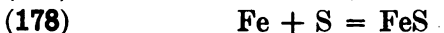
Under certain conditions even distinct polar compounds hydrolyse:



These polar compounds are called "strong" salts while the compounds enumerated in the list which have constituents near together in the displacement series, are termed "weak" salts. The former ionize strongly, the latter ionize but slightly if at all.

VI. COMBINATION

Combination is the union of two elements resulting in the formation of a compound: $\text{M} + \text{N} = \text{MN}$. While this equation apparently is the simplest type of reaction, it involves the principles of oxidation and reduction for M is usually oxidized and N is reduced. Ordinarily combination is called oxidation, and the reverse reaction is termed reduction. In a strict sense, however, combination as well as division involves oxidation *and* reduction. The common terminology, while practical in some respects, is thus ambiguous and should be avoided. Some examples of combination or "oxidation" are:



- (179) $4\text{Fe} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3$
 (180) $\text{N}_2 + 2\text{O}_2 = 2\text{NO}_2$
 (181) $\text{H}_2 + \text{F}_2 = 2\text{HF}$
 (182) $\text{P}_4 + 6\text{Cl}_2 = 4\text{PCl}_3$
 (183) $\text{W} + 3\text{Cl}_2 = \text{WCl}_6$
 (184) $\text{Bi} + 3\text{I} = \text{BiI}_3$
 (185) $3\text{Zn} + 2\text{Sb} = \text{Zn}_3\text{Sb}_2$
 (186) $3\text{Zn} + 2\text{As} = \text{Zn}_3\text{As}_2$

Not only metals and nonmetals combine, but also elements and compounds. The element in most cases is oxygen—therefore the obsolete term oxidation:

- (187) $\text{FeS} + 2\text{O}_2 = \text{FeSO}_4$
 (188) $\text{ZnS} + 2\text{O}_2 = \text{ZnSO}_4$
 (189) $2\text{NO} + \text{O}_2 = 2\text{NO}_2$
 (190) $4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} = 4\text{HNO}_3$
 (191) $4\text{MgO} + 2\text{CoO}_3 + \text{O}_2 = 4\text{MgCoO}_3$
 (192) $6\text{CO} + 6\text{K} = \text{C}_6\text{O}_6\text{K}_6$
 (193) $2\text{GaCl}_3 + \text{Ga} = 3\text{GaCl}_2$
 (194) $\text{Hg}(\text{NO}_3)_2 + \text{Hg} = 2\text{HgNO}_3$
 (195) $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe} = 3\text{FeSO}_4$

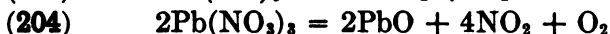
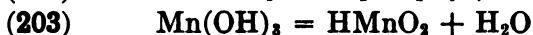
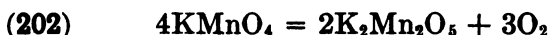
VII. DIVISION

Division, commonly called “reduction,” is the reverse reaction of combination, just as decomposition is the reverse of addition. Typical examples are:

- (196) $2\text{HCl} = \text{H}_2 + \text{Cl}_2$
 (197) $2\text{HgO} = 2\text{Hg} + \text{O}_2$
 (198) $\text{ZnCl}_2 = \text{Zn} + \text{Cl}_2$
 (199) $2\text{HI} = \text{H}_2 + 2\text{I}$

More complex compounds:

- (200) $\text{K}_2\text{PtCl}_6 = 2\text{KCl} + 2\text{Cl}_2 + \text{Pt}$
 (201) $4\text{CrO}_2\text{Cl}_2 = 2\text{Cr}_2\text{O}_3 + 2\text{Cl}_2 + \text{O}_2$



A related reaction is dissociation, that is, the breaking apart of molecules at higher temperature, while at lower temperature very often re-combination takes place (see Chapter 5). *Example:* At high temperature:

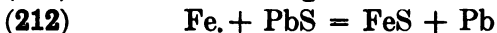
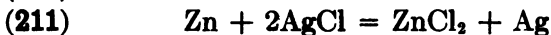
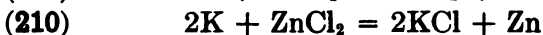
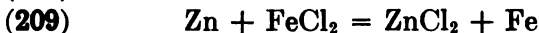


At low temperature:

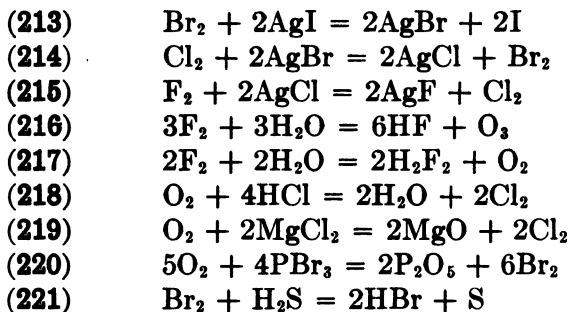


VIII. DISPLACEMENT

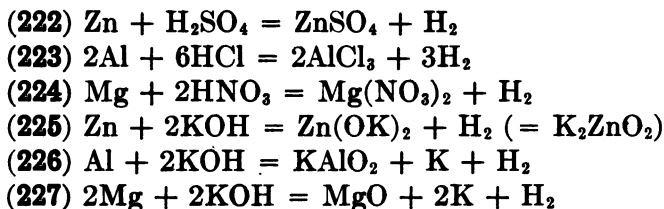
Displacement is a chemical reaction in which one element replaces another element in a compound. The general equation for metals is $\text{M} + \text{YX} = \text{MX} + \text{Y}$; for nonmetals $\text{N} + \text{YX} = \text{YN} + \text{X}$. Either a metal can replace another metal, or a nonmetal can replace another nonmetal. Displacement takes place when the metal, M, is more electro-positive than the metal, Y, or when the nonmetal, N, is more electro-negative than the nonmetal, X. The electro-positive or negative character of the elements is given in the displacement series (see appendix). Examples of this type of reactions are: Displacement by metals:



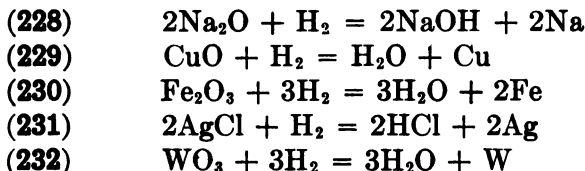
Displacement by nonmetals:



The many displacement reactions which involve hydrogen can be grouped into two types. In the first type of displacement the hydrogen of acids or bases is being replaced by a more electro-positive metal. In this case hydrogen is reduced and hence acts as an oxidizing agent:



In the other cases the hydrogen is oxidized, and so acts as a reducing agent:

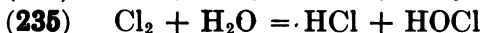
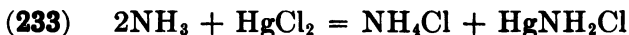


The first set of reactions (222–227), in which hydrogen is replaced by a metal, depends upon the electromotive force of the metal and the following general rule is deduced: Whenever the metal, M, is more positive

than hydrogen (see displacement series) it will take the charge from the hydrogen ion and liberate hydrogen gas, hence these metals are all soluble in acids according to the general equation $2M + 2H^+ = 2M^+ + H_2$.

IX. SUBSTITUTION

Substitution is a chemical reaction which resembles displacement; however, the element which interacts with a compound does not liberate the replaced element but combines with it according to the general type $2X + MN = XN + XM$ in the case of metals, and $2Y + MN = MY + NY$ in the case of nonmetals:

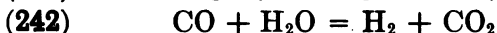
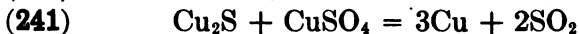


A related reaction is:

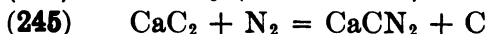
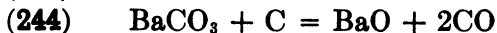
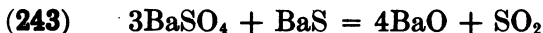


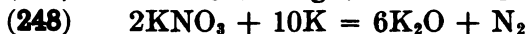
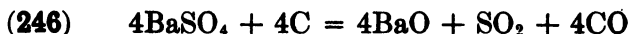
X. RESTITUTION

The reverse reaction of substitution is re-substitution or restitution, the general type being $MN + MY = M + NY$. To this class belong:



Similar and related reactions are:

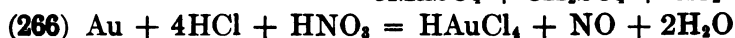
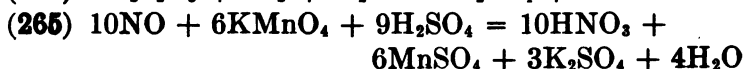
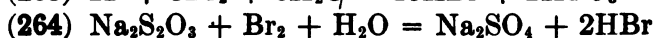
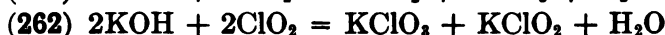
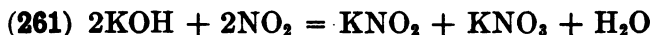
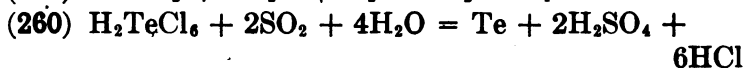
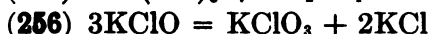
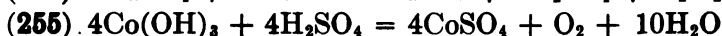
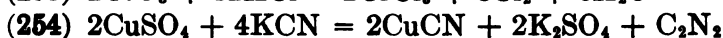
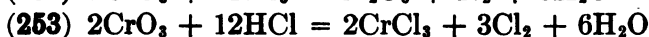
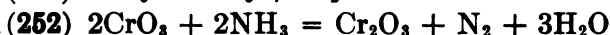
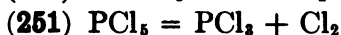
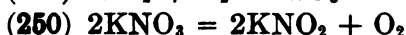


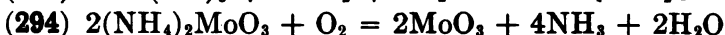
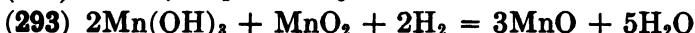
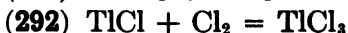
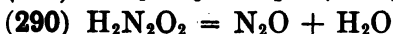
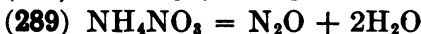
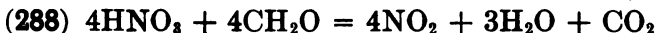
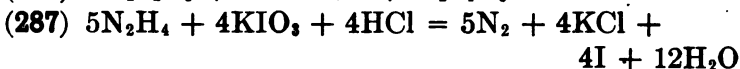
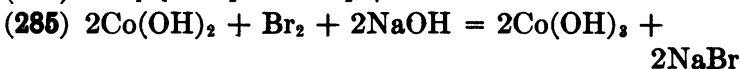
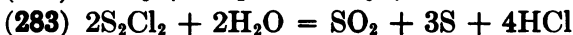
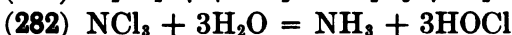
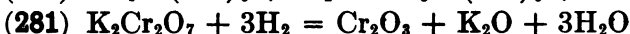
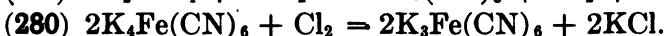
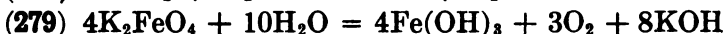
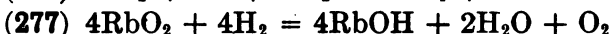
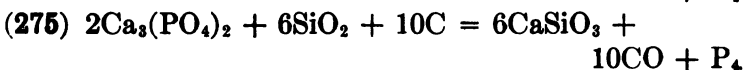
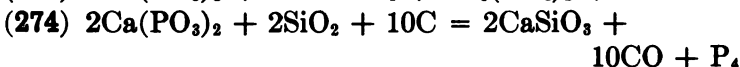
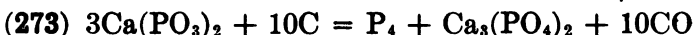
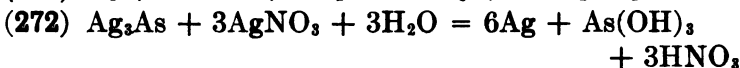
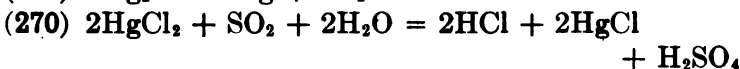
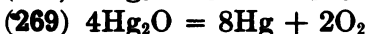


XI. OXIDATION AND REDUCTION

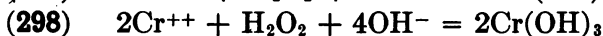
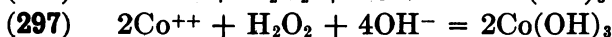
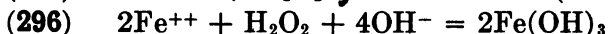
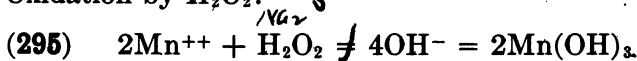
There are many reactions not classified under the previous titles which are characterized by oxidation and reduction. These reactions must be studied and in each case it should be determined which elements are oxidized and which are reduced, for only thus is it possible to get a clear conception of the meaning of oxidation and reduction.

A number of such reactions are:

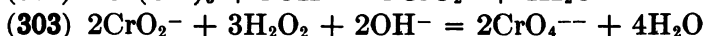
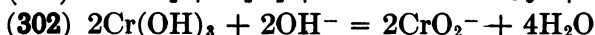
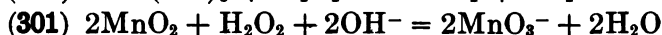




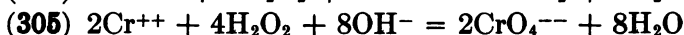
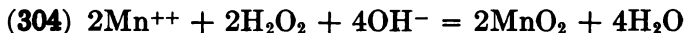
The above reactions are all in the non-ionic or molecular form; it is a helpful exercise to transcribe these equations into the ionic form in cases where the substances are ionized. Examples of typical ionic equations are: Oxidation by H_2O_2 :



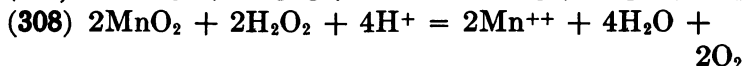
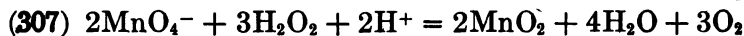
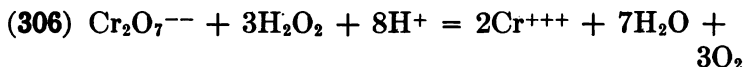
The metals Cr and Mn can be further oxidized:



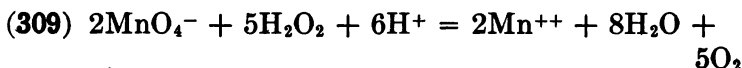
By adding the equations for manganese (295, 300) and chromium (298, 302, 303) together, the total equation of the reaction taking place becomes:



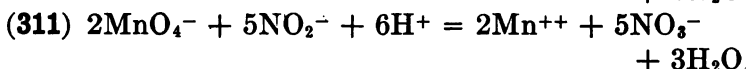
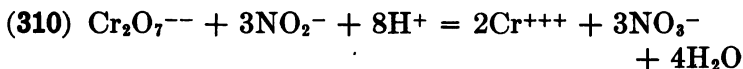
As shown by these equations, hydrogen peroxide will act as an oxidizing agent in alkaline solution. In acid solution, however, it will act as a reducing agent:



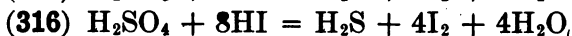
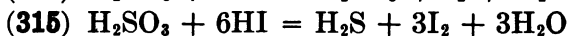
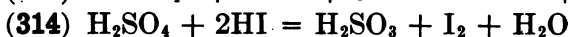
By adding the last two equations (307, 308) together, and cancelling MnO_2 which appears on both sides, the total equation becomes:



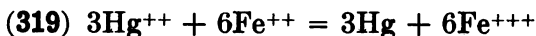
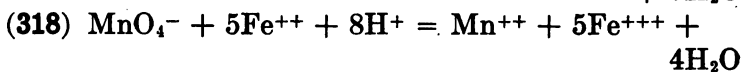
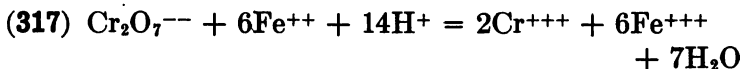
Reduction by NO_2^- :



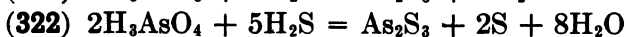
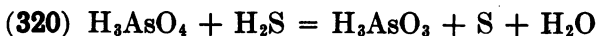
Reduction by HI :



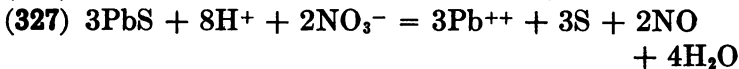
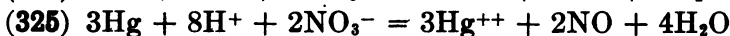
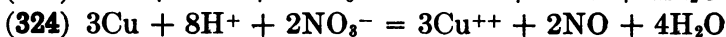
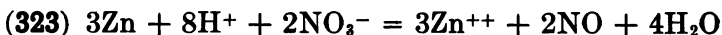
Reduction by Fe^{++} :



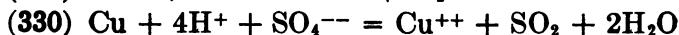
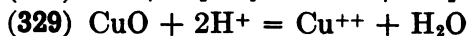
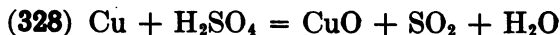
Reduction by H_2S :



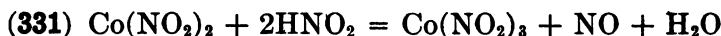
Oxidation by HNO_3 :



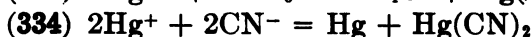
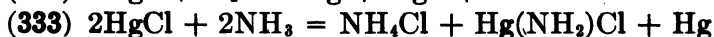
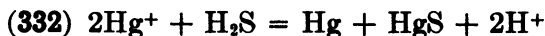
Oxidation by H_2SO_4 :



Oxidation by HNO_3 :



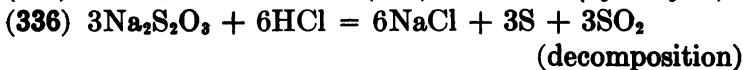
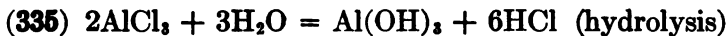
Oxidation and reduction of Hg^- :



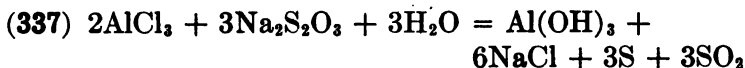
The student should devise laboratory experiments to prove the correctness of these reactions, and should be able to predict what will happen if certain chemicals react upon each other. He should tell whether the solutions must be acidified or made alkaline; he should know what color-changes or precipitations to expect, and be able to write the specific non-ionic equations for the above ionic reactions.

XII. COMPLEX REACTIONS

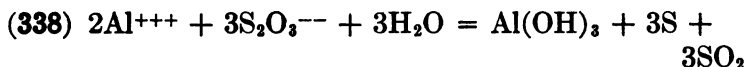
There are many cases in which the reaction products interact upon each other and produce a second set of reaction products. The equations of these reactions seem most complex when secondary reactions are included in a single equation; but this complexity disappears when more than one equation is written. The following shows the various steps of such reactions in different equations, and these, added together, form the equation of a complex reaction.



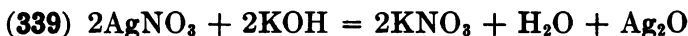
Added together and cancelling HCl leaves:



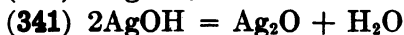
Reduced to the ionic form 337 becomes:



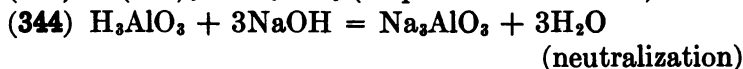
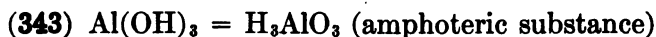
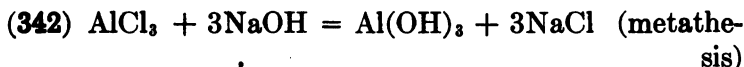
Likewise the reaction:



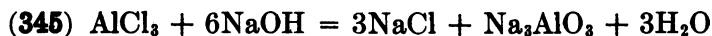
is composed of a metathesis and decomposition:



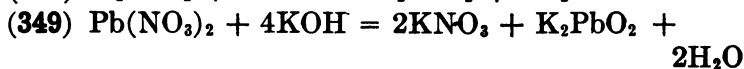
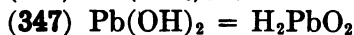
Other reactions of this type may involve amphoteric substances, as, for example:



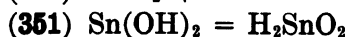
Adding these three equations together and cancelling the intermediate products gives:

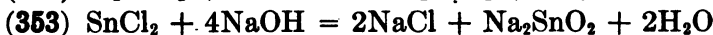


Similar equations are:

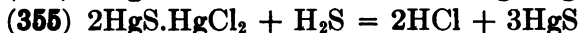
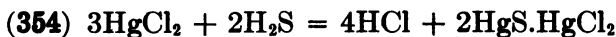


and

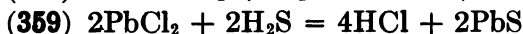
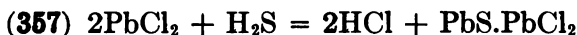




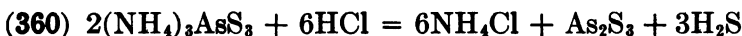
In a similar way some sulfides are formed:



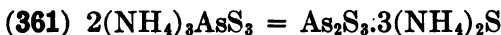
and



It may be that only a part of a double salt will react, and the resulting equation will appear complex, *e.g.*



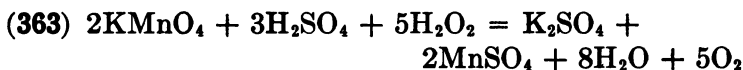
However, this equation becomes simple if the double salt is considered as composed of two salts, *e.g.*



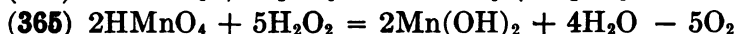
and one of these reacts:



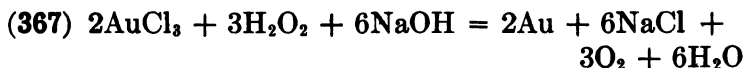
Other examples are



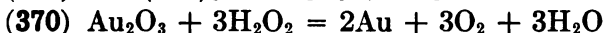
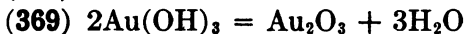
which is composed of the three steps:



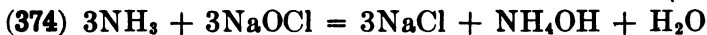
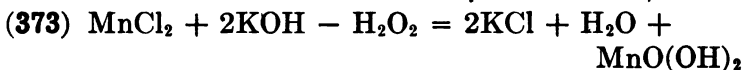
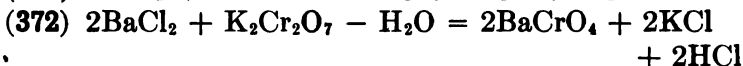
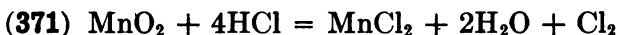
or again:



which consists of the three reactions:



In the following complex reactions two or more steps can be recognized, and accordingly two or more equations should be written for every case:



When problems involve a series of incomplete oxidations and reductions, it is well to construct separate equations for each reaction. An example of this type is offered by the following experiment: By adding sulfuric acid to potassium iodide a number of reaction products are formed. These reaction products are hydroiodic acid, iodine, sulfur, sulfur dioxide, and hydrogen sulfide besides potassium sulfate and water. It is impossible to see from a single equation the changes which have occurred, and each oxidation and reduction must be treated separately:

A. The formation of hydroiodic acid:



B. The formation of sulfur dioxide and iodine:



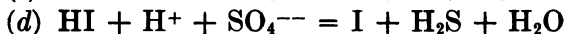
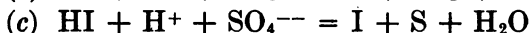
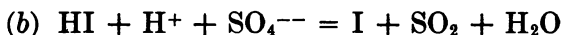
C. The formation of sulfur and iodine:



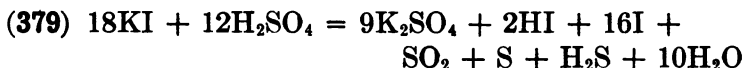
D. The formation of hydrogen sulfide and iodine:



These equations show that in *A* there is a simple metathesis, the replacement of a weaker acid by a stronger acid; in *B* the iodide is oxidized to iodine, and the hexavalent sulfur is reduced to tetravalent sulfur, in *C* to free sulfur, and finally in *D* to sulfide. It is quite possible that the reactions *B*, *C*, and *D*, are secondary reactions, as the HI formed in reaction *A* may be decomposed by the sulfuric acid. If such is the case the KI of the equations should be replaced by HI, and the unfinished equations are:

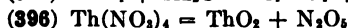
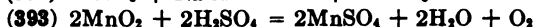
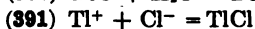
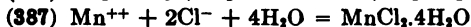
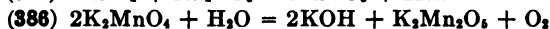


If the equations (375), (376), (377) and (378) are added the following "monster" equation results:

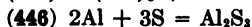
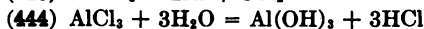
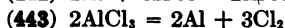
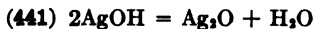


QUESTIONS AND PROBLEMS

1. Classify the following reactions according to type and note particularly whether oxidation and reduction is involved. If so, which elements are oxidized and which are reduced?



- (397) $\text{KMgCl}_2 = \text{KCl} + \text{MgCl}_2$
- (398) $\text{KOH} + \text{H}_2\text{S} = \text{H}_2\text{O} + \text{KSH}$
- (399) $\text{SiO}_2 + 2\text{CaF}_2 + \text{H}_2\text{SO}_4 = 2\text{CaSO}_4 + \text{SiF}_4 + 2\text{H}_2\text{O}$
- (400) $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$
- (401) $\text{CS}_2 + 3\text{O}_2 = \text{CO}_2 + 2\text{SO}_2$
- (402) $\text{B}_2\text{S}_3 + 6\text{H}_2\text{O} = 2\text{B(OH)}_3 + 3\text{H}_2\text{S}$
- (403) $\text{H}_3\text{BO}_3 = \text{HBO}_2 + \text{H}_2\text{O}$
- (404) $2\text{HBO}_2 = \text{B}_2\text{O}_3 + \text{H}_2\text{O}$
- (405) $\text{NaH}_2\text{PO}_4 = \text{NaPO}_3 + \text{H}_2\text{O}$
- (406) $2\text{Na}_2\text{HPO}_4 = \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$
- (407) $\text{BaO}_2 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{O}_2$
- (408) $\text{PbO}_2 + 4\text{HCl} = \text{PbCl}_4 + 2\text{H}_2\text{O}$
- (409) $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O}$
- (410) $\text{PbCl}_4 = \text{Cl}_2 + \text{PbCl}_2$
- (411) $\text{MnCl}_4 = \text{Cl}_2 + \text{MnCl}_2$
- (412) $2\text{HBr} + \text{H}_2\text{SO}_4 = \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
- (413) $\text{KBr} + \text{KClO}_3 = \text{KCl} + \text{KBrO}_3$
- (414) $2\text{I} + \text{H}_2\text{S} = 2\text{HI} + \text{S}$
- (415) $2\text{HCl} + \text{F}_2 = 2\text{HF} + \text{Cl}_2$
- (416) $2\text{AsH}_3 + 3\text{Na} = 2\text{Na}_3\text{As} + 3\text{H}_2$
- (417) $2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$
- (418) $6\text{F} + 3\text{H}_2\text{O} = 6\text{HF} + \text{O}_2$
- (419) $2\text{KI} + \text{O}_2 + \text{H}_2\text{O} = 2\text{KOH} + \text{I}_2 + \text{O}_2$
- (420) $\text{As}_2\text{O}_3 + 3\text{C} = \text{As}_4 + 3\text{CO}_2$
- (421) $4\text{SbCl}_3 + 6\text{H}_2\text{O} = \text{Sb}_2\text{O}_3 + 12\text{HCl}$
- (422) $2\text{Ga(NO}_3)_3 = \text{Ga}_2\text{O}_3 + 3\text{N}_2\text{O}_5$
- (423) $\text{NaNO}_2 + \text{Pb} = \text{NaNO}_2 + \text{PbO}$
- (424) $\text{Al}_2(\text{CO}_3)_3 = \text{Al}_2\text{O}_3 + 3\text{CO}_2$
- (425) $\text{Al}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 = 2\text{KAl(SO}_4)_2$
- (426) $\text{Al(OH)}_3 = \text{HAlO}_2 + \text{H}_2\text{O}$
- (427) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = \text{ZnSO}_4 + 7\text{H}_2\text{O}$
- (428) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = \text{Zn}^{++} + \text{SO}_4^{--} + 7\text{H}_2\text{O}$
- (429) $\text{ZnSO}_4 = \text{Zn}^{++} + \text{SO}_4^{--}$
- (430) $\text{Co(OOC)}_2 = \text{Co} + 2\text{CO}_2$
- (431) $\text{CoCO}_3 = \text{CoO} + \text{CO}_2$
- (432) $2\text{Cr(OH)}_3 + 3\text{H}_2\text{SO}_4 = \text{Cr}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$
- (433) $\text{CrO}_4^{--} - \text{Pb}^{++} = \text{PbCrO}_4$
- (434) $\text{Pb}^{++} + 2\text{I}^- = \text{PbI}_2$
- (435) $\text{PbCl}_4 + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{HCl}$
- (436) $\text{Te} + \text{SO}_2 = \text{TeO} + \text{SO}_2$
- (437) $\text{HAuCl}_4 = \text{AuCl} + \text{Cl}_2 + \text{HCl}$
- (438) $\text{HAuCl}_4 = \text{AuCl}_3 + \text{HCl}$
- (439) $\text{Ag}_2\text{O} + \text{H}_2\text{O} = 2\text{AgOH}$
- (440) $\text{Ag}^+ + \text{OH}^- = \text{AgOH}$



2. Write reactions (380) and (381) in the ionic form and deduce their general meaning and the experimental conditions.

3. Devise a laboratory experiment to prove the correctness of reactions (382), (389), (433), and 434.

4. Translate the meaning of reaction (387) into common language.

5. What is the difference between the reactions (407), (408) and (409)? What equation results if (408) is added to (410), and (409) is added to (411)?

6. Can you predict from the displacement series that the reactions shown in equations (414), (415), (418), (420), (384), and (416) will take place? On what grounds do you base your predictions?

7. What is the meaning of equations (427), (428) and (429), and what actual phenomena or reactions correspond to these equations?

8. Is there an essential difference between the reactions expressed in (430) and (431)?

9. What is the difference or similarity between (431) and (422), (426) and (427), (396) and (403) and (404)?

10. Compare equations (387) and (428) and state if either of these reactions is a reversible one?

11. What will happen if Br_2 is substituted for F_2 in reaction (415)? What will happen if HBr is taken instead of HCl ?

12. Write the complex reaction obtained by adding equations (437) and (438) together. Describe the experimental conditions.

13. What is the meaning of equations (439), (440), and (441)? Devise experiments for each reaction.

14. State in common terms the information contained in equations (442), (443), (444), (445). Suggest for each equation the experimental conditions under which the reaction takes place.

15. How will the speed of reaction (446) be affected if S is replaced by (a) Se, (b) Te, (c) O?

16. Why does the Te in (436) rob the S of a part of its O? Suggest an explanation.

17. What is the difference between equations (391) and (392)?

18. What takes place in the reactions expressed in equations (400) and (401)? Give a common term for the phenomena.

19. Does S replace O, or does O replace S in reaction (402)? Is this reaction in harmony with the displacement series?

APPENDIX I

KEY TO NOMENCLATURE OF CHEMICAL COMPOUNDS

This key to the nomenclature of inorganic compounds enables the beginner to construct numerous formulas of compounds whose names are given, and likewise to find the correct name for a given formula. It will also aid in finding possible reaction products in cases where a precipitate or a change of color occurs during the reaction.

To construct the formula for a compound it is only necessary to join the radicals or ions in such a way that all the valencies or charges are satisfied or neutralized. The formula for "cupric sulfate" is found by joining Cu^{++} (cupric ion) and SO_4^{--} (sulfate ion) to CuSO_4 . The formula for "ferric chromate" is found by joining 2Fe^{+++} (= six positive charges) with 3CrO_4^{--} (six negative charges) to $\text{Fe}_2(\text{CrO}_4)_3$. Likewise cupric chlorate requires Cu^{++} and 2ClO_3^- , that is $\text{Cu}(\text{ClO}_3)_2$. Cuprous phosphide is Cu_3P , and cupric phosphide is Cu_3P_2 .

By finding the ion or radical under the formulas the name of a given formula can be constructed: FeS shows iron to be bivalent (Fe^{++}), hence *ferrous sulfide*, while in Fe_2S_3 the iron is trivalent (Fe^{+++}), hence *ferric sulfide*. Likewise the formulas NaCl , NaClO_2 , NaClO_3 , NaClO_4 represent respectively sodium *chloride*, sodium *chlorate*, and sodium *perchlorate*.

The column indicating the color of the ion or radical is of advantage in laboratory work where the formation

Name of element, ions or radicals	Valence number	Symbol of			Color of ions
		Element	Cation	Anion	
Aluminum.....	0	Al			
aluminum ion.....	3		Al ⁺⁺⁺		
aluminate ion.....	3			AlO ₂ ⁻	
Ammonia.....	0	NH ₃			
ammonium.....	1		NH ₄ ⁺		
Antimony.....	0	Sb			
antimonous.....	3		Sb ⁺⁺⁺		
antimonic.....	5		Sb ⁺⁺⁺⁺⁺		
antimoniate.....	5			SbO ₃ ⁻	
antimonite.....	3			SbO ₂ ⁻	
Arsenic.....	0	As			
arsenous.....	3		As ⁺⁺⁺		
arsenic.....	5		As ⁺⁺⁺⁺⁺		
arsenide.....	3			As ^{'''}	
arsenite.....	3			AsO ₃ ⁻⁻⁻	
arsenate.....	5			AsO ₄ ⁻⁻⁻	
Barium.....	0	Ba			
barium.....	2		Ba ⁺⁺		
Bismuth.....	0	Bi			
bismuth.....	3		Bi ⁺⁺⁺		
bismuthyl.....	3	B		BiO ⁺	
Boron.....	0				
boron.....	3		B ⁺⁺⁺	BO ₂ ⁻⁻⁻	
borate.....	3			B ₄ O ₇ ⁻⁻⁻	
tetraborate.....	3				
Bromine.....	0	Br			
bromide.....	-1			Br ⁻	
bromite.....	-3			BrO ₂ ⁻	
bromate.....	-5			BrO ₃ ⁻	
Cadmium.....	0	Cd			
cadmium.....	2		Cd ⁺⁺		
Calcium.....	0	Ca			
calcium.....	2		Ca ⁺⁺		
Carbon.....	0	C			
carbide.....	4			C ^{'''}	
carbonate.....	4			CO ₃ ⁻⁻⁻	
bicarbonate.....	4			HCO ₃ ⁻	
Cerium.....	0	Ce			
cerous.....	3		Ce ⁺⁺⁺		
ceric.....	4		Ce ⁺⁺⁺⁺		
Chlorine.....	0	Cl			
chloride.....	-1			Cl ⁻	
hypochlorite.....	-1			ClO ⁻	
chlorite.....	-3			ClO ₂ ⁻	
chlorate.....	-5			ClO ₃ ⁻	
perchlorate.....	-7			ClO ₄ ⁻	
Chromium.....	0	Cr			
chromous.....	2		Cr ⁺⁺		blue
chromic.....	3		Cr ⁺⁺⁺		purple
chromite.....	3			CrO ₂ ⁻	green
chromate.....	5			Cr ₂ O ₇ ⁻⁻⁻	yellow
bichromate.....	5				orange
Cobalt.....	0	Co			
cobaltous.....	2		Co ⁺⁺		red
cobaltic.....	3		Co ⁺⁺⁺		(unstable)
Copper.....	0	Cu			
cuprous.....	1		Cu ⁺		colorless
cupric.....	2		Cu ⁺⁺		blue
copper ammonium.....	2		Cu(NH ₃) ₄ ⁺⁺		deep blue

Name of element, ions or radicals	Valence number	Symbol of			Color of ions
		Element	Cation	Anion	
Fluorine.....	0	F			
fluoride.....	-1			F ⁻	
Gold.....	0	Au			
aurous.....	1		Au ⁺		yellow
auric.....	3		Au ⁺⁺⁺		yellow
Hydrogen.....	0	H			
hydrogen.....	1		H ⁺		
hydride.....	-1			H ₂	
Iodine.....	0	I			
iodide.....	-1			I ⁻	
iodate.....	5			IO ₃ ⁻	
periodate.....	7			IO ₄ ⁻	
Iron.....	0	Fe			
ferrous.....	2		Fe ⁺⁺		green
ferric.....	3		Fe ⁺⁺⁺		yellow-brown
ferrate.....	6			FeO ₄ ⁻⁻	red
Lead.....	0	Pb			
plumbous.....	2		Pb ⁺⁺		
plumbic.....	4		Pb ⁺⁺⁺⁺		
plumbate.....	4			PbO ₃ ⁻⁻	
Lithium.....	0	Li			
lithium.....	1		Li ⁺		
Magnesium.....	0	Mg			
magnesium.....	2		Mg ⁺⁺		
Manganese.....	0	Mn			
manganous.....	2		Mn ⁺⁺		sl. pink
manganic.....	3		Mn ⁺⁺⁺		sl. green
manganate.....	5			MnO ₄ ⁻⁻	green
permanganate.....	7			MnO ₄	purple
Mercury.....	0	Hg			
mercurous.....	1		Hg ⁺		
mercuric.....	2		Hg ⁺⁺		
Nickel.....	0	Ni			
nickelous.....	2		Ni ⁺⁺		green
nickelic.....	3		Ni ⁺⁺⁺		(unstable)
Nitrogen.....	0	N			
nitride.....	-3			N ^{III}	
nitrite.....	3			NO ₂ ⁻	
nitrate.....	5			NO ₃ ⁻	
Oxygen.....	0	O			
oxide.....	-2			O ^{II}	
Phosphorous.....	0	P			
phosphide.....	-3			P ^{III}	
hypophosphite.....	1			H ₂ PO ₂ ⁻	
phosphite.....	3			H ₂ PO ₃ ⁻	
phosphate.....	5			PO ₄ ⁻⁻	
metaphosphate.....	5			PO ₃ ⁻	
monophosphate.....	5			H ₂ PO ₄	
pyrophosphate.....	5			P ₂ O ₇ ⁻⁻	
Platinum.....	0	Pt			
platinous.....	2		Pt ⁺⁺		yellow
platinic.....	4		Pt ⁺⁺⁺⁺		orange
Potassium.....	0	K			
potassium.....	1		K ⁺		

Name of element, ions or radicals	Valence number	Symbol of			Color of ions
		Element	Cation	Anion	
Silicon.....	0	Si		-	
silicide.....	-4			Si ^{iv}	
silicate.....	4			SiO ₄ ⁻⁻⁻⁻	
metasilicate.....	4			SiO ₃ ⁻⁻	
Silver.....	0	Ag			
silver.....	1		Ag ⁺		
Sodium.....	0	Na			
sodium.....	1		Na ⁺		
Strontium.....	0	Sr			
strontium.....	2		Sr ⁺⁺		
Sulphur.....	0	S			
sulphide.....	-2			S ⁻⁻	
hydrosulphide.....	-2			HS ⁻⁻	
sulfit.....	4			SO ₃ ⁻⁻	
bisulfit.....	4			HSO ₃ ⁻⁻	
sulfate.....	6			SO ₄ ⁻⁻	
bisulfate.....	6			HSO ₄ ⁻	
Tin.....	0	Sn			
stannous.....	2		Sn ⁺⁺		
stannite.....	2			SnO ₃ ⁻⁻	
stannic.....	4		Sn ⁺⁺⁺⁺		
stannate.....	4			SnO ₃ ⁻⁻	
Zinc.....	0	Zn			
zinc.....	2		Zn ⁺⁺		
zincate.....	2			ZnO ₂	
zinc ammonium.....	2		Zn(NH ₃) ₄ ⁺⁺		
Uranium.....	0	U			
uranous.....	2		U ⁺⁺		light green
uranyl.....	6		UO ₂ ⁺⁺		yellow
uranate.....	6			UO ₄ ⁻⁻	yellow
<i>Common Organic Radicals</i>					
acetates (CH ₃ COO ⁻).....	1			Ac ⁻	
cyanides.....	1			CN ⁻	
cyanates.....	1			CNO ⁻	
ferrocyanides.....	4			Fe(CN) ₆	
ferricyanides.....	3			Fe(CN) ₆	
oxalates (ooo) ₂ ⁻⁻	2			Ox ⁻⁻	
rhodanates.....	1			CNS ⁻	

of a distinctive color in the test tube will show the respective ion or compound. Thus, if during a chemical reaction, the yellow solution of a chromate turns green—chromic ion has been formed, if the purple permanganate solution turns green—manganate ion has been produced, and so on. Where no color is given the substance is colorless or white.

If necessary the student may enlarge the list to meet special requirements. A frequent use of this key in the laboratory is recommended.

APPENDIX II

DISPLACEMENT SERIES

(Elements printed in capitals to be memorized by the student)

In the displacement series the elements are arranged according to their electro-motive force, that is, the capacity of holding the ionic charges more or less firmly.

NEGATIVE

fluorine
CHLORINE
OXYGEN
NITROGEN
BROMINE
IODINE
SULFUR
selenium
tellurium
PHOSPHORUS
chromium
vanadium
tungsten
molybdenum
CARBON
boron
GOLD
osmium
platinum
iridium

tantalum
palladium
ruthenium
rhodium
ANTIMONY
BISMUTH
ARSENIC
MERCURY
SILVER
COPPER
silicon
titanium
HYDROGEN
TIN
LEAD
germanium
zirconium
cerium
nickel
cobalt
thallium

columbium
cadmium
IRON
ZINC
manganese
uranium
gadolinium
indium
gallium
ALLUMINIUM
rare-earth metals
beryllium
scandium
yttrium
MAGNESIUM
lithium
CALCIUM
strontium
BARIUM
SODIUM
POTASSIUM
POSITIVE

At the top of the list are the most negative elements which displace all following anions. The elements near the end of the list are the most positive and will displace each cation above them. Thus Br will displace I and S, but F will displace Cl and Br. Ca will displace Mg, Al, and Fe, but K will displace Na and Ca, etc.

The farther apart the elements, the more stable their compounds. Thus KF is the most stable compound, while a compound of O and F is so unstable that it cannot exist.

APPENDIX III

THE PERIODIC SYSTEM AND THE CLASSIFICATION OF THE ELEMENTS

A systematical arrangement of all chemical elements is essential for an understanding of their correlation, their similarity or difference. The periodic system is such a classification in which all elements are logically tabulated. The position occupied by an element in this system is an indication of its chemical and physical properties.

The periodic system was not suddenly *discovered* as is often stated, but has gradually developed and taken form with increasing chemical knowledge during the last 100 years. One of the earliest attempts at classification was made in 1829 by Doebereiner who arranged some elements in *triads* or groups-of-three, such as Ca-Sr-Ba, Li-Na-K, Cl-Br-I, etc.; because the properties and the atomic weight in each triad show a certain relationship. The same idea was further developed by Cooke in 1854 and by DeChancourtois in 1865. The next noteworthy step was taken in 1867 by Newlands in his *octaves* or groups-of-eight in which he pointed out, that if all elements are arranged according to increasing atomic weights, each eighth element has analogous properties, for elements of similar properties are separated by seven others, just as is the case in a harmonious musical scale. This law of octaves contained the nucleus of the periodic system and in 1869 Mendeleeff and Lothar Meyer, working independently of each other,

presented the first table of a system of elements which was generally accepted. Mendeleeff predicted the properties of three unknown elements from three empty spaces occurring in his table, and when these elements were later discovered, it was found that his predictions came true with an astounding accuracy. Since that time numerous discoveries have been made and the system has gradually been completed. Today we may assume with great confidence that only five elements remain undiscovered and that the total number of elements in the series from hydrogen to uranium inclusive is 92. The five unknown elements with atomic numbers 43, 61, 75, 85, and 87 would complete the table.

If all elements are arranged in the order of increasing atomic weights, then the 92 elements between H (At. No. 1) and U (At. No. 92) inclusive are divided into six periods, the terminals of each period being the noble gases. Thus there are in:

Period I, extending from He to Ne	8 elements ($= 2 \times 2^2$)
Period II, extending from Ne to Ar	8 elements ($= 2 \times 2^2$)
Period III, extending from Ar to Kr	18 elements ($= 2 \times 3^2$)
Period IV, extending from Kr to Xe	18 elements ($= 2 \times 3^2$)
Period V, extending from Xe to Nt	32 elements ($= 2 \times 4^2$)
Period VI, extending from Nt to U	7 elements

Each period has the following characteristics:

The terminals of each period are electrically neutral (noble gases).

The first three elements of each period are strongly electropositive (light metals).

The last three elements of each period are strongly electronegative (non-metals).

The central members of each period are amphoteric (heavy metals).

The members of the carbon family are the framework

of the system and form a transition between the different groups of elements (C the life-element, Si the rock-forming element).

Besides the *horizontal* division into *periods* there is the *vertical* division into *groups*. The general rule of the periodic chart is:

The similarity among the elements in the upper half

The Periodic System

NON-METALS				INERT ELEMENTS				LIGHT METALS				
Group	4	5a	6a	7a	0	1a	2a	3a	4a			
	Carbon group	Phosphor group	Sulfur group	Halogen group	Noble gases	Alkali group	Earthalkali group	Earth metals	Carbon group			
Period Vb	82 Pb	83 Bi	84 Po	85	86 Nt	87	88 Ra	89 Ac	90 Th	VI		
IVb	50 Sn	51 Sb	52 Te	53 I	54 Xe	55 Cs	56 Ba	57 La	58 Ce	Va		
IIIb	32 Ge	33 As	34 Se	35 Br	36 Kr	37 Rb	38 Sr	39 Y	40 Zr	IVa		
IIb	14 Si	15 P	16 S	17 Cl	18 Ar	19 K	20 Ca	21 Sc	22 Ti	IIIa		
Ib	6 C	7 N	8 O	9 F	10 Ne	11 Na	12 Mg	13 Al	14 Si	IIa		
0	1 H				2 He	3 Li	4 Be	5 B	6 C	Ia		
Iron period III'	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	Iron period III'
Silver period IV'	40 Zr	41 Nb	42 Mo	43	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	Silver period IV'
Rare earth metals V''	58 Ce 59 Pr 60 Nd 61 Sm 62 Eu 63 Gd 64 Tb 65 Dy 66 Ho 67 Er 68 Db 69 Tm 70 Yb 71 Lu 72										Rare earth metals V''	
Gold period V'	72 Lu	73 Ta	74 W	75	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	Gold period V'
Radioactive elements VI	90 Th	91 Bv	92 U									
Group	4	5b	6b	7b	8	8	8	1b	2b	3b	4	

HEAVY METALS

of the table is most pronounced in the vertical direction, therefore these elements possess group-analogy.

The similarity among the elements of the lower half of the table is most pronounced in the horizontal direction, therefore these elements possess period-analogy.

ATOMIC NUMBERS AND ATOMIC WEIGHTS

Importance of the elements is indicated by * and o. The atomic numbers serve as an index to the periodic table.

Actinium.....	89	Ac		Neodymium.....	60	Nd	144.3
* Aluminum.....	13	Al	27.1	Neon.....	10	Ne	20.2
Antimony.....	51	Sb	120.2	o Nickel.....	28	Ni	58.68
Argon.....	18	A	39.88	* Nitrogen.....	7	N	14.01
Arsenic.....	33	As	74.96	Osmium.....	76	Os	190.9
o Barium.....	56	Ba	137.37	* Oxygen.....	8	O	16.000
Beryllium.....	4	Be	9.1	Palladium.....	46	Pd	106.7
o Bismuth.....	83	Bi	208.0	* Phosphorus.....	15	P	31.04
o Boron.....	5	B	11.0	o Platinum.....	78	Pt	195.2
Brevium.....	91	Bv		Polonium.....	84	Po	
o Bromine.....	35	Br	79.92	* Potassium.....	19	K	39.10
Cadmium.....	48	Cd	112.4	Praseodymium.....	59	Pr	140.9
Caesium.....	55	Cs	132.81	o Radium.....	88	Ra	226.0
* Calcium.....	20	Ca	40.07	Rhodium.....	45	Rh	102.9
* Carbon.....	6	C	12.00	Rubidium.....	37	Rb	85.45
Cerium.....	58	Ce	140.25	Ruthenium.....	44	Ru	101.7
* Chlorine.....	17	Cl	35.46	Samarium.....	62	Sm	150.4
o Chromium.....	24	Cr	52.0	Scandium.....	21	Sc	44.1
o Cobalt.....	27	Co	58.97	* Selenium.....	34	Se	79.2
Columbium.....	41	Cb	93.1	* Silicon.....	14	Si	28.3
o Copper.....	29	Cu	63.57	o Silver.....	47	Ag	107.88
Denebium.....	69	Db	168.5	* Sodium.....	11	Na	23.00
Dysprosium.....	66	Dy	162.5	o Strontium.....	38	Sr	87.63
Erbium.....	68	Er	167.5	* Sulfur.....	16	S	32.06
Europium.....	63	Eu	152.0	Tantalum.....	73	Ta	181.5
o Fluorine.....	9	F	19.0	Tellurium.....	52	Te	127.5
Gadolinium.....	64	Gd	157.3	Terbium.....	65	Tb	159.2
Gallium.....	31	Ga	69.9	Thallium.....	81	Tl	204.0
Germanium.....	32	Ge	72.5	o Thorium.....	90	Th	232.4
Gold.....	79	Au	197.2	Thulium.....	70	Tm	170.5
o Helium.....	2	He	4.00	o Tin.....	50	Sn	118.7
* Hydrogen.....	1	H	1.008	o Titanium.....	22	Ti	48.1
Indium.....	49	In	114.8	Tungsten.....	74	W	184.0
Iodine.....	53	I	126.96	o Uranium.....	92	U	238.2
Iridium.....	77	Ir	193.1	Vanadium.....	23	V	51.0
* Iron.....	26	Fe	55.84	Xenon.....	54	X	130.2
Krypton.....	36	Kr	82.92	Ytterbium.....	71	Yb	173.5
Lanthanum.....	57	La	139.0	Yttrium.....	39	Y	88.7
o Lead.....	82	Pb	207.2	o Zinc.....	30	Zn	65.37
Lithium.....	3	Li	6.49	Zirconium.....	40	Zr	90.6
Lutecium.....	72	Lu	175.0				
* Magnesium.....	12	Mg	24.32				
o Manganese.....	25	Mn	54.93				
o Mercury.....	80	Hg	200.6				
Molybdenum.....	42	Mo	96.0				

Gl (glucium) is Be (Beryllium)
 Nb (niobium) is Cb (Columbium)
 Fl is F; Xe is X; Yt is Y.
 As (asote) is N; J (jod) is I.

Accordingly there are group-relations and period-relations. *E.g.* the group-relation of Au refers to its properties which are similar to those of Ag and Cu, while the period-relation of Au refers to those properties which resemble Hg and Pt; in other words, gold has a group similarity to silver and copper, and a period similarity to mercury and platinum.

OUTLINE OF PROPERTIES OF ELEMENTS AS DEDUCED FROM THE PERIODIC TABLE

In the UPPER half of the table are the elements of the strongest e.m.f., the simplest spectra, low density, and colorless ions.

In the LOWER half of the chart are the elements of the weakest e.m.f., complex spectra, high density, and colored ions.

On the LEFT of the table are the electro-negative elements which form the acids. The solid elements are brittle and paramagnetic.

On the RIGHT of the table are the electro-positive elements forming the bases. The solid elements are malleable.

In the LEFT UPPER HALF and RIGHT LOWER HALF are located the non-metals and heavy-metals which are found in their native form in nature (free state). Their sulfides are common and they are readily reduced to the free state.

In the RIGHT UPPER HALF and LEFT LOWER HALF are the light metals and heavy metals which always occur in combination and never in their free state in nature. Their oxides and oxysalts are common, and it is with difficulty that they are reduced to free elements. Not all elements are of equal importance. Fourteen elements are of primary importance (marked

with bold type and *) for they constitute 99 per cent of the known earth surface and are abundant in the lithosphere, hydrosphere, atmosphere. These elements are essential to all living matter (biosphere) and are of fundamental importance in every industry. About 40 elements are of secondary importance (marked o), for they are less abundant and are used only for specific purposes in industry and technic. About 33 elements are of more or less scientific interest only for they very rarely occur and are of little or no present use.

The student must be familiar with the fourteen important and fundamental elements, know their position in the table, and be familiar with their chemistry, for they are most common on the surface of our earth and their compounds are used in every industry, in every material science, and in every-day life. Elementary chemistry confines itself mainly to these elements as they are the basis for a study of the other elements. Thus, *e.g.* with chlorine as type or example, the properties of fluorine, bromine, and iodine can readily be memorized; while with sulfur as type or example the characteristics of selenium and tellurium are easily learned; potassium and sodium is the type for lithium, rubidium, and cesium; manganese is similar to chromium, iron similar to cobalt and nickel—and so on.

REFERENCES

Classification of chemical elements, Scientific American Supplement, vol. 87, p. 146, 1919.

Modification of the periodic table, Am. Jour. of Science, vol. 46, p. 481, 1918.

Distribution of chemical elements, Science Progress, vol. 14, p. 602, 1920.

BOOKS ON THE SUBJECT:

Rudorf, G., The Periodic System.

Garrett, A. E., The Periodic Law.

APPENDIX IV

SOLUBILITY TABLE OF COMPOUNDS

(To be Memorized by Students)

SOLUBLE in water:

- ALL CHLORIDES, except AgCl , PbCl_2 , HgCl_2 ;
- ALL NITRATES, except bismuth, subnitrate;
- ALL SULFATES, except barium sulfate, strontium sulfate, calcium sulfate, lead sulfate;
- ALL ACETATES, except basic ferric acetate and basic aluminum acetate;
- ALL ALKALI SALTS, except acid potassium tartrate, acid ammonium tartrate, potassium platin chloride, ammonium platin chloride, and sodium pyroantimoniate.

INSOLUBLE in water:

- | | | |
|---|---|--|
| ALL OXIDES | } | except those of the alkalies
and earth alkali metals; |
| ALL SULFIDES | | |
| ALL HYDROXIDES | | |
| ALL CARBONATES | } | except those of the alkali
metals; |
| ALL PHOSPHATES | | |
| ALL SILICATES | | |
| ALL CHROMATES, except those of the alkalies;
Ca, Sr. | | |

SOLUBILITY TABLE OF COMPOUNDS

(for reference)

ACETATES are SOLUBLE, except AgAc , HgAc , HgAc_2 .

ARSENITES are INSOLUBLE, except those of the alkalies.

ARSENATES are INSOLUBLE, except those of the alkalies and the acid arsenates of the earth alkali metals.

BORATES are SOLUBLE.

BROMATES are SOLUBLE, least soluble are HgBrO_3 , AgBrO_3 .

BROMIDES are SOLUBLE, except CuBr , AgBr , HgBr_2 , PbBr_2 .

CARBONATES are insoluble, except those of alkalies and Ti .

CHLORATES are SOLUBLE, except HgClO_3 .

CHLORIDES are SOLUBLE, except AgCl , HgCl , CuCl , AuCl , PtCl_2 , PbCl_2 .

CHROMATES are INSOLUBLE, except those of alkalies and CaCrO_4 , SrCrO_4 and MgCrO_4 .

CYANIDES are INSOLUBLE, except those of alkalies and earth alkalies.

FERROCYANIDES are INSOLUBLE, except those of alkalies and earth alkalies.

FERRICYANIDES are INSOLUBLE, except those of alkalies and earth alkalies.

FLUORIDES are INSOLUBLE, except those of alkalies and AgF , FeF_2 , SnF_2 , SrF_2 and CdF_2 .

IODATES are INSOLUBLE, except those of alkalies.

IODIDES are SOLUBLE, except AgI , CuI , HgI_2 , PbI_2 , BiI_3 , SbI_3 , Pt metals.

MANGANATES are INSOLUBLE, except those of the alkalies.

MOLYBDATES are INSOLUBLE, except those of the alkalies.

NITRATES are SOLUBLE.

NITRITES are SOLUBLE, except AgNO_2 .

OXALATES are **INSOLUBLE**, except those of the alkalies.

PERMANGANATES are **SOLUBLE**, except AgMnO_4 .

PHOSPHATES are **INSOLUBLE**, except those of the alkalies.

PHOSPHITES are **INSOLUBLE**, except those of the alkalies, and Tl.

SILICATES are **INSOLUBLE**, except those of the alkalies.

SULFATES are **SOLUBLE**, except BaSO_4 , SrSO_4 , PbSO_4 , slightly soluble are Ca, Ag, Hg.

SULFIDES are **INSOLUBLE**, except those of the alkalies.

APPENDIX V

PREPARATION OF SALTS

A Metallic Salt May be Prepared in Any One of the Following Ways (To be Memorized by the Student)

Reaction between:

1. METAL and HALOGEN:



- 1a. METAL and ACID:



2. METAL-OXIDE and ACID-ANHYDRIDE:



- 2a. METAL-OXIDE and ACID:



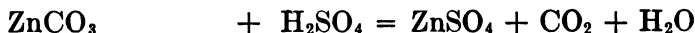
3. METAL HYDROXIDE and ACID ANHYDRIDE:



- 3a. METAL HYDROXIDE and ACID:



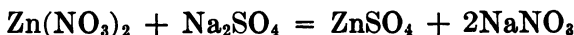
4. METAL CARBONATE and ACID:



5. METAL SULFIDE and ACID:



6. Interaction of two METAL SALTS:



KEY TO THE EQUATIONS

The following is a systematic index of the equations used in this book. The numbers to the left of the formula refer to the reacting substances (which stand at the left of an equation), and the numbers to the right refer to reaction products (which stand at the right side of an equation).

This index makes it possible to find at a glance how some of the substances are prepared—thus under oxygen there is a score of equations showing how this gas may be made. It also gives the analytical tests for many compounds, that is, the reactions used for their detection. Furthermore it will facilitate the construction of similar equations for reactions taking place with related elements. Thus many reactions given under sulfur occur also with selenium and tellurium, likewise those of arsenic compounds have a relation to those of antimony and bismuth compounds.

It is well for students to make a comparative study of reactions by consulting the periodic system and the displacement series and extend this index to the laboratory and lecture note book for further reference.

ALUMINUM

442, 446.....	Al		443
21, 338.....	Al ⁺⁺⁺		
162, 335, 337, 342, 345, 443, 444	AlCl ₃		113-5, 442, 445
113.....	Al ₂ O ₃		424
114.....	Al ₂ S ₃		127, 446
115.....	Al ₂ Se ₃		
116.....	Al ₂ Te ₃		
131.....	Al ₄ C ₃		
9, 15, 127, 343, 344, 426, 445.	Al(OH) ₃	20, 21, 131, 162, 335, 337 338, 342, 444	
.....	H ₂ AlO ₃		343
.....	HAIO ₂		426

.....	$\text{Al}(\text{NO}_3)_3$	9
20, 425.....	$\text{Al}_2(\text{SO}_4)_3$	
424.....	$\text{Al}_2(\text{CO}_3)_3$	
.....	AlPO_4	15

AMMONIUM

86, 88, 89, 92, 233, 333, 374..	NH_3	101, 106, 168, 282, 294
46.....	NH_4^+	
90, 91.....	NH_4OH	46, 86, 374
92, 101.....	NH_4Cl	88, 233, 333, 360, 362
289.....	NH_4NO_3	
94, 95, 96, 362.....	$(\text{NH}_4)_2\text{S}$	361
360, 361.....	$(\text{NH}_4)_2\text{AsS}_3$	94
.....	$(\text{NH}_4)_2\text{SnS}_3$	95, 96
289.....	$(\text{NH}_4)_2\text{MoO}_4$	

ANTIMONY

185.....	Sb	
165, 421.....	SbCl_3	
.....	Sb_2O_3	421
80, 81.....	Sb_2S_3	
.....	Sb_2S_5	150
.....	SbOCl	165

ARSENIC

186.....	As	420
416.....	AsH_3	118, 169
420.....	As_2O_3	
94.....	As_2S_3	321, 322, 360
321.....	H_3AsO_3	272, 320
320, 322.....	H_3AsO_4	

BARIUM

18, 139, 140.....	Ba^{++}	151
17, 372.....	BaCl_2	407
.....	BaO	243, 244, 246
151, 407.....	BaO_2	
157, 243.....	BaS	
.....	BaC_2	247
7, 13.....	$\text{Ba}(\text{OH})_2$	157, 158
158.....	$\text{Ba}(\text{SH})_2$	157
.....	$\text{Ba}(\text{NO}_2)_2$	7
243, 246.....	BaSO_4	17, 18, 139
244, 247.....	BaCO_3	

APPENDIX

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.....	BaCrO ₄	140, 372
.....	Ba ₃ (PO ₄) ₂	13

BERYLLIUM

390.....	BeO	
.....	Be(OH) ₂	390

BISMUTH

184.....	Bi	
160.....	BiCl ₃	
.....	BiI ₃	184
.....	Bi(OH) ₃	161
161.....	BiOCl	160

BORON

.....	B ₂ O ₃	133, 404
402.....	B ₂ S ₃	
168.....	BN	106
404.....	BO(OH)	168, 403
133, 403.....	B(OH) ₃	402
106.....	B(NH ₂) ₃	

BROMINE

54, 213, 221, 263, 264, 285...	Br	27, 31, 32, 33, 53, 214, 220, 412
27, 33, 53.....	Br ⁻	54
31, 32, 383, 412.....	HBr	221, 263, 264

CADMIUM

388.....	CdCl ₂	
----------	-------------------	-------

CALCIUM

73, 177.....	Ca	70
399.....	CaF ₂	123, 124
75, 77.....	CaCl ₂	6, 76, 110, 111, 112, 177
70, 74, 79, 84, 110, 120, 123.	CaO	69, 73
.....	CaS	120, 121
112.....	Ca ₃ P ₂	
169.....	Ca ₃ As ₂	
130, 245.....	CaC ₂	
6, 12, 76.....	Ca(OH) ₂	77, 84, 130, 169
.....	CaCN ₂	245
.....	CaSO ₄	12, 399
69, 121.....	CaCO ₃	74, 75, 79

124.....	CaSiO_3	274, 275
273, 274.....	$\text{Ca}(\text{PO}_3)_2$	
275.....	$\text{Ca}_3(\text{PO}_4)_2$	273

CARBON

244, 246, 247, 258, 273, 276, 420.....	C.....	245
.....	C_2H_2	130
234, 400.....	CH_4	131
167.....	CCl_4	
192, 242.....	CO.....	246, 244, 258, 273, 274, 275
71, 79.....	CO_2	20, 21, 69, 134, 242, 288, 400, 401, 420, 430, 431
127, 401.....	CS_2	
145-7, 334.....	CN^-	
.....	C_2N_2	254
.....	CH_2Cl	234
288.....	CH_3O	
.....	COCl_2	167
.....	COCl	276

CHLORINE

27, 53, 177, 182, 183, 214, 234, 276, 280, 292.....	Cl_2	196, 198, 200, 201, 215, 218, 219, 251, 253, 371, 410, 411, 415, 437, 443
387, 391.....	Cl^-	27, 53
2, 4, 6, 8, 19, 110, 118, 196, 223, 287, 371.....	HCl.....	101, 119, 234, 235, 283, 284, 372, 421, 443
262.....	ClO_2	
.....	HOCl	235, 282

CHROMIUM

298, 305.....	Cr^{++}	
.....	Cr^{+++}	35, 306, 310, 312, 317
303.....	CrO_2^-	302
140, 382, 433.....	CrO_4^{--}	25, 303, 305
25, 35, 281, 306, 310, 312, 317, 372.....	$\text{Cr}_2\text{O}_7^{--}$	
.....	CrCl_3	253
.....	Cr_2O_3	201, 252, 268, 281
252, 253.....	CrO_3	
301, 302, 432.....	$\text{Cr}(\text{OH})_3$	298
201.....	$\text{Cr}(\text{OCl})_2$	
.....	$\text{Cr}_2(\text{SO}_4)_3$	432

COBALT

.....	Co		430
142, 297.....	Co ⁺⁺		
.....	CoO		431
191.....	CoO ₃		
285.....	Co(OH) ₂		142
255.....	Co(OH) ₃		285, 297
331.....	Co(NO ₂) ₂		
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—they are strongly electro-positive; form bases; are univalent.....	110
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- SULFUR GROUP** are the elements of the sixth group of the periodic system: O, S, Se, Te. 111
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